THE GEOCHEMISTRY AND PHOSPHORUS SORPTION CHARACTERISTICS OF MGENI CATCHMENT SEDIMENTS

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PREFACE

The experimental work described in this thesis was carried out in the Department of Geological Sciences, University of Cape Town, Rondebosch, from August to October, 1994, under the supervision of Dr M V Fey of the Department of Geological Sciences.

These studies represent original work by the author and have not been submitted for degree purposes to another University. Where use was made of the work of others it has been acknowledged in the text.

Signed by candidate

R S Hounsome

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ABSTRACT

The Mgeni River is vital for the continued industrial and social development of Durban and Pietermaritzburg and the river has been impounded in four places to provide a crucial water resource to these areas. The river is highly susceptible to anthropogenic pollution, particularly phosphorus, which may be derived from unsanitised peri-urban areas or run-off from fertilised agricultural lands. Sediments may be sources or sinks of pollution in aquatic systems.

Grab samples of the uppermost sediment layer were taken from sites at each of the impoundments and analysed for salient geochemical characteristics, such as major and trace element concentrations, clay mineralogy, organic carbon, P fractionation, and particle size distribution. Batch experiments were also carried out to determine the P sorption/desorption characteristics of the sediments under different pH and redox conditions.

The sediments are dominated by clay sized material (< 2mm) which is composed of kaolinite, gibbsite, goethite, mica and other undifferentiated 2:1 layer silicates and quartz. Kaolinite, gibbsite and goethite are found extensively throughout the catchment area and are the result of intense weathering. These minerals readily sorb cations onto their surfaces. The significant correlations which were found between the clay content and the concentration of trace metals, particularly Mo, Pb, and Zn, most likely result from accumulations of cations on the mineral surfaces. It was suggested, therefore, that the Mgeni sediments are potential sinks for polluting elements.

The P sorption experiments resulted in the construction of sorption isotherms which were described by a single point index derived by extrapolating the amount of P sorbed from a 1 mg/l equilibrium P concentration. The indices correlated significantly with concentrations of Al_2O_3, Fe_2O_3 and clay in the sediment, suggesting that P sorption reactions are most likely to be influenced by these sediment properties. This suggestion is supported by experimental evidence which shows that with increased pH there is a noticeable decrease in the sorption capacity of the sediments, a response which would be expected if sorption was onto surfaces of variable charge which would be influenced by the presence of hydroxyl or hydrogen ions on the surfaces. The influence of redox on P sorption is mostly confined to a control on the solubility of Fe_2O_3 in the sediments, i.e. the reduction of ferric to ferrous iron. Ferric iron oxides are the species onto which P is preferentially sorbed.

By nature of the laboratory experimental conditions, precipitation of P minerals was unlikely to have occurred. Therefore, precipitation modelling was carried out using the MINTEQA2 geochemical equilibrium model utilising water quality data from the Inanda inlet sampling site. The calculated equilibrium conditions showed that the solubility of P was consistant with control by the Ca-phosphate minerals, hydroxyapatite and fluorapatite. It is likely that this would remain the *status quo* unless there was a significant drop in pH, below 6.4, or an increase in the activity of P.

It was not possible to conclude whether sorption or precipitation was likely to be the most influential process in removing P from solution so that it was no longer available for biological uptake.

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INTRODUCTION

The continued development of the major metropolitan regions of Kwazulu-Natal is dependent on a sustained and reliable water resource. In order to meet these demands Umgeni Water, the organisation which manages the Mgeni Catchment, has embarked on a management plan to ensure the continuation of a high quality water supply. The Mgeni Catchment Water Quality Plan represents the first step by this organisation to address the problem of supplying clean water to the region. A location map of the study area in relation to the major metropolitan areas in Southern Africa is depicted in Fig. 1.

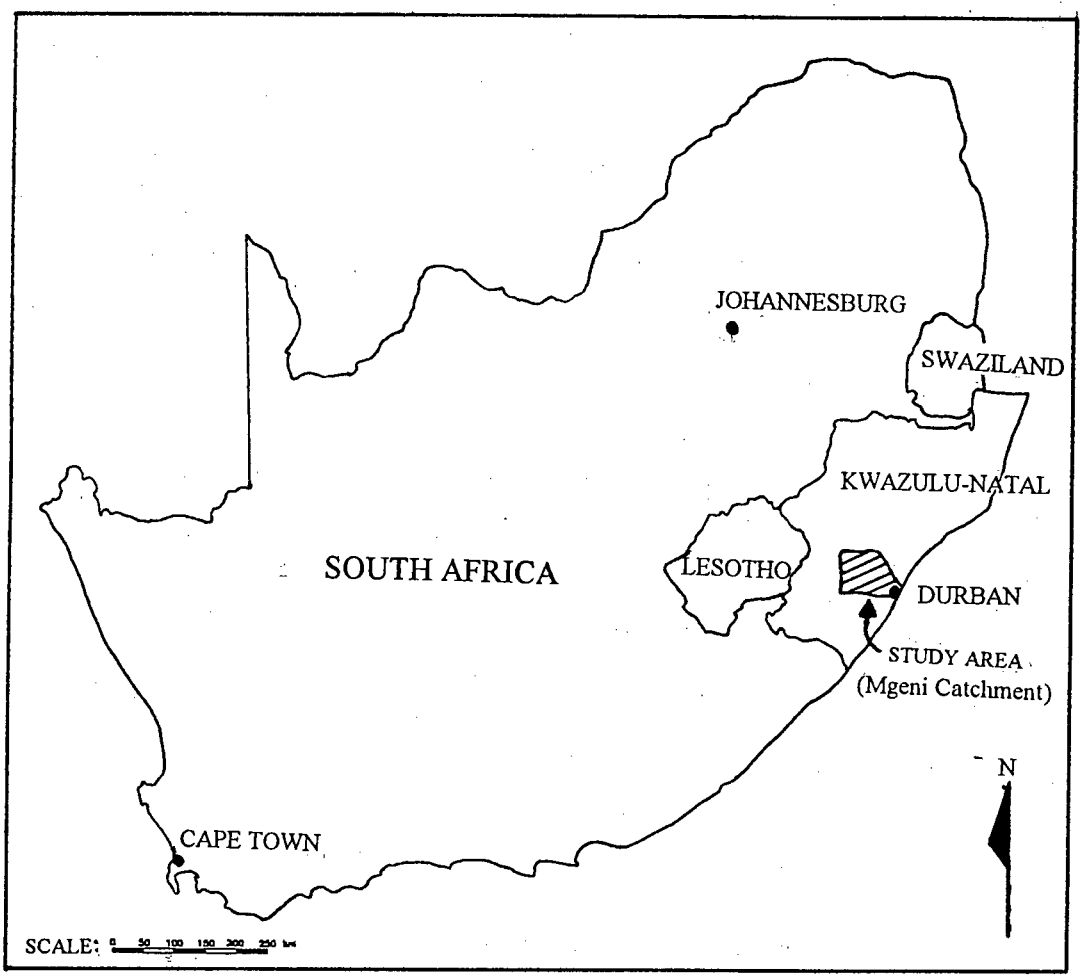


Figure 1 The location of the study area in relation to the major metropolitan areas in South Africa.

The Mgeni Catchment is highly susceptible to a number of potential water pollution problems. The catchment is influenced by the presence of industry and, potentially more importantly, by peri-urban development. A feature of this development is that it is informal and often poorly sanitised, resulting in a high potential for contaminated water supplies. On the one hand, faecal contamination will result in the infection of the river with coliform bacteria, and, on the other hand, it will result in an increased load of phosphorus finding its way into the stream. The added influence of run-off from fertilised agricultural lands contributes a further source of P into the river (Dallas & Day, 1993).

Phosphorus has been recognised worldwide as an important pollutant because it is the limiting nutrient in the process of eutrophication, which is defined as the nutrient enrichment of a water body. The term eutrophication does not necessarily imply any response from the aquatic system, although it is generally accepted that nutrient enrichment results in the accelerated growth of algae and other aquatic plant life (Moss, 1980). Such biological responses significantly reduce the quality of an impoundment, from both a water quality and aesthetic point of view.

The susceptibility of the Mgeni impoundments to potential eutrophication problems is a concern in terms of water quality and aesthetics. The consequences of decreasing water quality will be recognised in the increased cost of water purification, while the decrease in the aesthetic quality of the water bodies is almost as important since the Natal Parks Board manages three and potentially four of the impoundments as recreational facilities.

Umgeni Water, recognising the importance of P to the sustained quality of the impoundments, commenced a desk-top study of the interactions which could influence the distribution of P between dissolved, precipitated and adsorbed phases in the impoundments (Pillay *et al.*, 1993). The study utilised the MINTEQA2 geochemical speciation model. The results of the speciation indicated that the reactions of P would result in that element co-precipitating with other elements, or sorbing onto minerals present in the water. The net result of these reactions would be that the P present in the system would effectively be removed from solution, so that it was no longer available for biological utilisation.

The use of MINTEQA2 is, however, limited in this type of study because it requires a number of assumptions to be made about the nature of the system. This is especially true for the adsorption model which has a database that is too limited for extensive application. The use of a specific adsorption model also requires an understanding of the nature of the adsorption sites.

In view of the limited application and potential problems associated with modelling P in the impoundments a research project was initiated, in an attempt to further understand the interactions between P and sediments in the impoundments. The findings of that project are presented in this thesis.

An understanding of the sediment/P interactions in freshwater systems firstly requires that geochemical characterisation of the sediments be carried out. Förstner & Wittman (1979) note that sediments may be used to detect pollution in aquatic systems. The analytical results may, therefore, be used as base-line values for the sediments in the area and may be applied as comparisons for the detection of future pollution events.

The geochemical characterisation could also be applied to understanding the nature of sediment/P interactions, which were experimentally determined, in the system. Such an understanding could be used as an improvement of the MINTEQA2 modelling procedure, allowing refined assumptions to be input into the programme. The results of the refined modelling may then be applied directly to specific impoundments.

CHAPTER 1

A REVIEW OF SEDIMENT-PHOSPHORUS INTERACTIONS IN FRESHWATER ENVIRONMENTS

1.1 Eutrophication and the role of phosphorus

The role of phosphorus in aquatic systems has been well studied throughout the world. P is the limiting nutrient in the process of eutrophication (Valiela, 1991). Eutrophication simply describes the nutrient enrichment of a waterbody (Dallas & Day, 1993); it is a qualitative term which does not suggest any specific biological reaction to the increase in nutrients (Moss, 1980). Generally though, it is accepted that the effect of eutrophication is the accelerated growth of algae and other aquatic plant matter. The growth of algae can significantly reduce the quality of an impoundment. Davies & Day (1986) note that when algae die they are often washed ashore and form foul smelling masses of decaying material which seriously diminish the aesthetic value of impoundments. Hayes & Burch (1989) noted that algae have been implicated in the production of odours which have been given descriptions such as "geranium, grassy, cucumber, fishy and spicy". The odours in drinking water often give rise to consumer complaints. Davies & Day (1986) state that decaying algal remains use up large amounts of oxygen in the water, resulting in fish mortality through suffocation. This takes place during warm weather when microbial decomposition of the algal biomass uses up oxygen too rapidly. Similar observations have been noted by Rossi & Premazzi (1991) while studying P in Lake Varese, Italy.

Although it was initially believed that by limiting anthropogenic C, N and P supply algal growth could be controlled, it has subsequently been found that only P is effectively limiting for algal growth in aquatic systems. Carbon and nitrogen supply can be augmented from the atmosphere (Moss, 1980; Schindler, 1991; Semmelink, 1990).

Phosphorus is one of the essential nutrients for sustaining plant growth because it plays an important role in energy transfer mechanisms within cell systems, as well as constituting several proteins, enzymes, nucleic acids and metabolic substances (Ahlgren, 1988; Semmelink, 1990).

The dominant species of P in the aqueous environment is orthophosphate (o-PO_4^{3-})[1] and its distribution will depend on the pH of the aquatic system (Holtan *et al.*, 1988).

Organic and inorganic complexes of P will also occur in the aqueous environment but in lesser proportions than the o-PO_4^{3-} species (Walmsley & Butty, 1980 in Semmelink, 1990). Of the species of P in aqueous systems orthophosphate is the only species of P available for uptake by algae, i.e. bioavailable P (Boström *et al.*, 1988a). Bioavailable P refers to the sum of P that is immediately available and P that can be transformed into a readily accessible form by naturally occurring processes (Boström *et al.*, 1988a).

Eutrophication is a natural process, and the tendency of impounded freshwater bodies is one that proceeds towards a eutrophic state (*pers comm.* J Day), a condition in which the potential concentration of nutrients is high (Hutchinson, 1969). This suggests that although there may be low nutrient concentrations in solution, the total concentrations are high because the whole supply is locked up elsewhere, for example in the sediments. The tendency is, however, a slow one. The impact of human kind on a water body is one of increasing the rate of eutrophication, a process which has been termed "cultural eutrophication" (Grizzard *et al.*, 1982; Rossi & Premazzi, 1991).

Dallas & Day (1993) note that there are certain factors which will naturally contribute P to a freshwater system, including climatic and catchment characteristics. Anthropogenic sources, those which contribute to "cultural eutrophication", include point and diffuse sources. Table 1.1 summarises the sources of nutrients.

In South Africa, where the effects of eutrophication are significant, a 1 mg/l P effluent standard was legislated in 1985 (Grobler, 1985; Grobler & Silberbauer, 1985; Grobler, 1988).

[1] P will be used in future to represent the o-PO_4^{3-} species, unless otherwise specified

Table 1.1 Potential sources of P in freshwater bodies

Sources		
Climatic	weathering of rocks and soils	
	erosion	
	rainfall	
	variability of runoff	
Catchment characteristics	surface geology	
	land form	
Anthropogenic	point sources	sewage effluent
		industrial discharge
		intensive animal cultivation
		detergents
	diffuse sources	agricultural runoff, after the addition of fertilisers and the disturbance of the soil mantle
		urban runoff
		peri-urban runoff

(modified from Dallas & Day, 1993)

It was hoped that by enforcing the standard there would be an 80 to 90 % reduction of the point source P load (Grobler, 1988). It was estimated by Taylor *et al.* (1984) (in Grobler, 1988) that point source P contributes about 60 % of the total P in reservoirs.

The P standard has been criticised in that it does not take into consideration the P receiving capacity of individual reservoirs (Pretorius, 1983; Grobler & Silberbauer, 1985), nor does it consider the important effects of diffuse sources of P. Furthermore, the P standard does not consider the effects of internal P loading. Weichers & Heynike (1986) and Breen & Twinch (1983) note that lake bottom sediments can be an important non-point source of P. In defence of the standard, however, similar P restrictions instituted in the early 1970's have resulted in significant water quality improvements in Lake Erie (Cooley, 1993).

To understand the impact of internal P loading it is prudent to look at P cycling in a reservoir. P, in varying amounts and forms, is almost continually transported to reservoir bottoms by sedimentation (Forsberg, 1989). Biological, physical, chemical and mechanical processes, will result in P being returned to solution (Forsberg, 1989). P release from sediments would, therefore, affect water quality (Shaw & Prepas, 1990a). These sediment fluxes may be significant, especially when the water P concentration is less than the equilibrium concentration of the sediment (Weichers & Heynike, 1986).

Boström *et al.* (1988b) distinguished the major mechanisms of P deposition. These include sedimentation of organic and inorganic allochthonous material, surficial biotic uptake, adsorption to sediment particles, and complexation with inorganic compounds in water. For a detailed discussion of P cycling the reader is directed to Håkanson (1993). A detailed description on the role of biota in P cycling may be found in Granéli & Solander (1988) and Andersson *et al.* (1988).

1.2 The role of sediment in phosphorus cycling

P reactions with sediment are characterised by two processes, Dolan *et al.* (1981). The first describes the removal of P from solution, a process known as sorption. The second process (desorption) is characterised by a release of P from the sediments into solution. Sediments, therefore, may act as a sink or source of P in lakes (Moore *et al.*, 1991). The fundamental principle

which describes P sorption/desorption is one of equilibrium. Froelich (1988) describes the equilibrium state as: "At equilibrium between sorbed and dissolved P, the rates of the forward reaction (sorption) and the reverse reaction (desorption) are the same. If the concentration of dissolved P were to be increased by some external process, then more P would sorb onto surfaces to re-establish the equilibrium conditions. If the concentration were to fall by being withdrawn from solution the P would be released from the solids."

1.2.1 Sediment P sorption

Berkheiser *et al.*'s (1980) definition of sorption has been employed in this discussion. They define a sorption reaction as one in which P is removed from solution through its concentration in a solid phase. This may involve the reversible physical sorption process, or alternatively chemisorption, which is partially or completely irreversible. Precipitation involves the removal of two, or more, components from a solution by their combination into a new solid-state compound. For the purposes of this project, precipitation is incorporated into the sorption definition as most researchers have been unsuccessful in experimentally differentiating between the two mechanisms (Froelich, 1988; He *et al.*, 1991; Holtan *et al.*, 1988; Moore *et al.*, 1991).

A number of factors have been mentioned as being important in terms of P sorption. These include: P concentration, pH and pE, clay fraction of the sediment, depth of the water, concentration of other ions and organic matter, temperature of the water, particle surface area, and microbial activity (Fox *et al.*, 1989; Keulder, 1982, Moore *et al.*, 1991; Singh & Gilkes, 1991). Although microbial activity has been noted as influencing P sorption, and its influence has been discussed by authors such as Doremus & Clesceri (1982), its effect is limited. A number of authors, including Donald & Meisheng (1988), Lucotte & d'Anglejan (1988) and Pagnotta *et al.* (1989), have noted that sediment-P interactions are predominately physico-chemical rather than biological.

1.2.1.1 Role of sediment inorganic species

The presence of aluminium and iron in the sediment is possibly the most important influence on P sorption (Borggaard *et al.*, 1990). P can become extremely strongly adsorbed onto iron hydroxide particles. The reaction has been described by Sposito (1989) as taking place when a hydroxyl group in the mineral goethite (iron hydroxide) is protonated to form a Lewis acid site. It can then be exchanged to allow the formation of an inner-sphere complex with the ligand HPO_4^{2-}. The surface complex is detailed in the reaction:

$$Fe\text{-}OH_2 + HPO_4^{2-} \rightarrow FeOPO_2OH + H_2O \quad \text{(from Mott, 1989)}$$

HPO_4^{2-} is bound through its oxygen pairs to a pair of adjacent Fe^{3+} cations (Sposito, 1989) forming a binuclear complex. For this reason, crystal faces having adjacent hydroxyl groups will be the ones onto which HPO_4^{2-} is preferentially absorbed (Colombo *et al.*, 1994). In the case of goethite, the surface arrangement of hydroxyl ligands on the principal (110) crystal faces, making up 90% of the crystal surface (Colombo *et al.*, 1994), are exactly compatible with HPO_4^{2-} and as such binuclear complexes have been demonstrated (Mott, 1989). Consequently goethite has a relatively consistent P adsorption capacity (Colombo *et al.*, 1994), which approaches a theoretical 2.51 mmol P m^{-2} for the binuclear complex on the (110) face. Similar adsorption is possible at pairs of Al-OH sites and particularly with gibbsite (Mott, 1989).

Distinct correlation between P sorption and Fe and Al hydroxide content in sediments has been noted by Istvánovics *et al.* (1989) and Borggaard (1983).

Phosphorus sorption onto Fe and Al hydroxide surfaces will predominate under acidic pH conditions, and the stability of the complexes decreases as pH increases to a point where the Ca-phosphate minerals are more stable (Tisdale *et al.*, 1985).

1.2.1.2 The role of sediment clay fraction

Most of the phosphorus sorption capacity in soils is due to the sediment's finest fractions (Holtan *et al.*, 1988). This is to be expected because the active surface area increases with decreasing particle size. Because of this a positive correlation is often found between P sorption and clay content.

Holtan *et al.* (1988) suggest that two mechanisms are responsible for P sorption to clay minerals. The first occurs at low P concentrations; P is sorbed by replacement of water molecules at the edge of a clay lattice rather than by exchange with a hydroxyl group. The second reaction, occurring at higher concentrations, describes sorption by displacing clay structural silicate. Fox & Malati (1993) studied four clay types: kaolin, mica, vermiculite and smectite, and noted that no sorption differences could be distinguished between the minerals, although, it would be expected that the 1:1 layer aluminosilicates would have a higher sorption capacity because of the presence of cations in interlayer spacings and surface hydroxyl groups (Sposito, 1984).

1.2.1.3 Role of sediment organic matter

Organic matter may influence sorption in two ways, it may either increase P sorption or may block sorption sites (Holtan *et al.*, 1988). An increase in sorption is due to organic materials inhibiting the crystallization of Fe and Al oxides and, therefore, increasing their sorption characteristics (Borggaard *et al.*, 1990). Prevention of P sorption has been attributed to competition for adsorption sites (Borggaard *et al.*, 1990). Chavarria (1981) has shown that the P sorption capacity of clay was reduced in the presence of organic matter.

Organic surface functional groups are also sites for P sorption (Sposito, 1984).

1.2.1.4 Role of pH

pH is another important control of the P ligand reaction (Mott, 1988). This would be expected in a mechanism involving hydroxyl surface species. Wild (1988) notes that P sorption is greatest at pH 3-5. This observation is supported by Mott (1988) who states that the greatest amount of P sorption occurs at the pH equal to the first ionisation constant (pK_1) of the anion. This is explained by the three ionization states of orthophosphate, Table 1.2. As pH is increased the valence of the P state also increases and adsorption declines steeply (Mott, 1988).

Table 1.2 Ionization constants of orthophosphate species in solution

Species in solution	Ionization constants (at 25°C)
H_3PO_4, $H_2PO_4^-$	$pK_1 = 2.1$
HPO_4^{2-}, PO_4^{3-}	$pK_2 = 7.2$
HPO_4^{2-} complexes	$pK_3 = 12.3$

(from Snoeyink and Jenkins, 1980)

Sorption-pH dependence may also be attributed to the relationship between pH and the electrostatic potential of the absorbing plane (Barrow, 1984). As pH increases the charge on the adsorbing plane is likely to decrease thus decreasing the tendency for P sorption. The pH dependency will depend on P occurrence, as Ca-phosphates are more stable than Fe- and Al-phosphates at high pH conditions.

P sorption will also influence the pH of a solution (Barrow, 1984). Barrow (1984) suggests that this is due to the charge conveyed to the surface by P sorption. When this charge is less than the average charge of the ions in solution, sorption will increase the pH. This is caused by a net release of hydroxide ions from the surface. The opposite is true for the case where charge imparted to the surface is greater than the average charge on ions in solution.

1.2.1.5 Effect of temperature

Holtan *et al.* (1988) credit large changes in water temperature as being influential in *o*-PO_4^{3-} sorption reactions. Large positive temperature differences, in the region of 5°C, may enhance maximum sorption capacity by as much as 30% (Holtan *et al.*, 1988). Kwari & Batey (1991) observed significant increases in soil P sorption after heating the soil. Opposite trends were observed by Boers & van Hese (1988) and Kelderman & van de Repe (1982). These authors noticed enhanced P release from lake sediments with an increase in temperature. They stated that enhanced microbial and chemical reactivity could be responsible for their observations. Barrow (1979) notes that temperature increases may serve to increase both sorption and desorption rates.

1.2.1.6 Methods of P sorption study

Phosphorus sorption characteristics of sediments are most often displayed in terms of sorption isotherms. Sorption isotherms have one basic criteria, that the quantity of P in solution is a function of the initial concentration and the sorbed concentration (Holtan *et al.*, 1988). Sorption isotherms may be described in terms of four models based on the following equations: Langmuir, Freundlich, Tempkin, and the best-fit-model (Barrow, 1978). The benefits and drawbacks of each of the models will not be discussed here as they will be covered in Chapter 3.

Studies of sorption isotherms by Barrow (1983), Froelich (1988) and Fox *et al.* (1989) have shown that P sorption is a two step procedure. The first step is a rapid process influenced by surface area and charge balance and will often account for 50-90% of the total sorption (Froelich, 1988). The second, slower step is dependent on the chemical composition of the solid phase.

Sediments containing Fe and Al hydroxides will display a greater slow sorption capacity (Froelich, 1988). Completion of the slower sorption stage, to a state of equilibrium, is seldom achieved in the laboratory. Barrow & Shaw (1975) noted that sorption continued for a period of 1000 days, i.e. that equilibrium conditions did not occur. P sorbed during the slow stage is not readily desorbed (Barrow, 1983). This has been shown in that sorption and desorption isotherms do not coincide. "Sorption has therefore been described as irreversible" (Barrow, 1983).

1.2.2 Sediment P desorption

Phosphorus sorption is not irreversible as is evident from the large body of literature which describes P desorption processes. Desorption is induced by a variety of environmental changes, including redox conditions, pH, temperature, P concentration, microbial activity and sulphur concentrations (Callender, 1982; Caraco *et al.*, 1989; Fox *et al.*, 1989; Furumai *et al.*, 1989; Marsden, 1989; Shaw & Prepas, 1990b). A change in redox and pH conditions are considered to be most important.

1.2.2.1 Redox controlled release

A change in sediment conditions from an oxic to an anoxic state may be brought about by an increase in biological oxygen demand (Marsden, 1989). The respiration requirements of the aquatic organisms may result in strongly reducing conditions and anoxic/anaerobic sediments (Marsden, 1989). It has been stated that Fe^{3+}-P complexes dominate the insoluble P forms, therefore, reducing conditions will reduce the ferric complexes to ferrous complexes. This reduction will bring both the Fe and P into solution (Furumai & Ohgaki, 1989; Marsden, 1989; Pagnotta *et al.*, 1989; van der Molen, 1991).

Evidence of aerobic release, as suggested by Lennox (1984), has not been shown experimentally. It is suggested that aerobic release is not linked to chemical desorption processes but is associated with physical processes occurring at the sediment-water interface. Marsden (1989) suggests that an oxic zone develops immediately above the anoxic zone in a sediment. By rapidly oxidising the Fe^{2+}, the zone will effectively prevent the release of P into the overlying water column. If, however, this oxidised zone is disturbed, either through physical (e.g. seasonal lake turnover, or climatic flushing) or biological (e.g. bioturbation, or microbiological activity) processes (Callender, 1982; Marsden, 1989), then P may be released into the water column. In deep lakes these processes are likely to be limited.

1.2.2.2 pH controlled release

High pH levels in water are likely to bring about release of P from sediments. A high pH may be produced by enhanced photosynthetic activity (Boers, 1991), which may withdraw CO_2 from the water and affect the $CO_2/HCO_3^-/CO_3^{2-}$ equilibrium which controls pH, resulting in increased pH. Sondergaard (1989) details an extreme example of photosynthetic pH increase in Lake Sobygaard (Denmark) where pH increased to between 10 and 11. pH increase will decrease the P-binding capacity of inorganic ions and clays, principally because OH^- ions will replace P on the adsorption sites (Boström *et al.*, 1988b).

Furumai *et al.* (1989) noted that maximum release took place at pH 8 and Petterson & Boström (1986) noted maximum release at pH 10, although Boers (1991) believes that enhanced desorption

will take place at even higher pH values which were difficult to achieve in the laboratory without greatly enhancing the solution alkalinity and influencing the process. High pH may enhance precipitation of calcium P complexes in hard waters, therefore reducing the amount of P available for bio-uptake and limiting the net concentration of P in solution (Boström *et al.*, 1988b; Marsden, 1989).

1.2.2.3 Sulphate concentration

Caraco *et al.*'s (1989) arguments for SO_4^{2-} controlled release are linked to the pre-mentioned processes. Essentially Caraco *et al.* (1989) believe that SO_4^{2-} could either compete with P for ligand adsorption sites, or alternatively the reduction of SO_4^{2-} in anoxic sediments can elevate pH and diminish P sorption capacity of iron hydroxides. Tisdale *et al.* (1985) suggest that although SO_4^{2-} is specifically sorbed it is unable to cause the release of much P. Phosphorus forms a stronger bond at surfaces than SO_4^{2-}.

1.2.2.4 Microbial, temperature and nitrate controlled release

The influence of temperature, nitrates and microbial activity are closely linked. Microbial activity is enhanced at high temperatures (Marsden, 1989). This enhancement will result in an increased reduction of the oxidised surface layer and increased P release (Marsden, 1989; Boström *et al.*, 1988b). Microbial activity will also be enhanced where nitrate concentrations are high (Jansson, 1986; Jensen & Andersen, 1992). Microbial activity is most influential in increasing the oxygen consumption and decreasing the redox potential (Boström *et al.*, 1988b).

1.2.2.5 Bio-uptake

Biological processes have largely been ignored in the preceding discussion, however, their role should not be discarded in terms of P cycling in freshwater lakes. Biota would be expected to remove P from the water column and will play an intricate role in terms of P available for sorption or desorption processes. Biological processes fall outside the scope of this project and will not be dealt with any further.

1.3 Conclusion

Phosphorus is an important aquatic pollutant, particularly for catchments which drain highly populated, unsanitised areas, or fertilised agricultural land. The aquatic response to P pollution is the accelerated growth of algae and other aquatic plant matter which can significantly reduce the quality of the impoundment from an aesthetic and water quality viewpoint.

In South Africa, a 1 mg/l P standard was set to try and limit the effects of P pollution. The standard is restrictive because it does not take the nature of the individual impoundment into consideration. These are very important considerations because reservoir sediments may be sources or sinks of P, i.e. P may sorb onto or desorb from sediment surfaces, depending on the characteristics of the sediment particles and on the nature of the aqueous system.

Phosphorus sorption will preferentially take place onto Fe or Al oxides, or clay mineral surfaces, especially in oxidised, acidic environments. In more alkaline conditions Ca-phosphate minerals are more stable. Phosphorus desorption may result after the onset of different environmental conditions, such as a change to more reducing conditions or an increase in pH.

It is evident that there are a number of factors which are related to the P sorption capacity of a sediment. The characteristics of the sediment and therefore the catchment area from where the sediments were derived are very important. It is necessary to analyse the sediment material and determine which of the sediment's characteristics is most likely to influence its P sorption capacity and to experimentally describe the sediment/P interactions. The combination of these two studies should permit some geochemical understanding of the P sorption capacity of the sediment.

CHAPTER 2

GEOCHEMICAL CHARACTERISATION OF MGENI CATCHMENT SEDIMENTS

2.1 Introduction

In order to determine the P sorption characteristics and differences between samples it is necessary to describe the sediments in terms of their physical and chemical properties. To assess which properties of the sediments have the greatest control on P sorption and to determine the geochemical significance of the sediments, a comprehensive geochemical characterisation was carried out. In an attempt to assess the regional significance of the results, a detailed description of the study area was also undertaken.

Such appreciation is not only useful in understanding the P sorption properties of the sediments but is also valuable as a base-line, or background, study of the chemical nature of the impoundments. When integrated with a detailed understanding of the chemical inter-relationships which are likely to influence water quality in the impoundments, such a study will provide a basis for the future monitoring and detection of pollution problems in the impoundments.

Such a base-line study of the sediments is essential in areas which are most likely to be influenced by anthropogenic sources of pollution - such as the Mgeni Catchment. Förstner & Wittman (1979) stress the importance of a base-line study by noting the significance of sediments, rather than water quality, in assessing pollution. In an ideal situation, Förstner & Wittman (1979) envisage being able to detect pollution sources long after input has taken place. The processes of sorption, precipitation, and organic bonding tend to accumulate pollutants in the fine grained fraction of sediments. This is particularly useful from an analytical point of view since the element concentration in sediments could be from 1000 to 10000 times higher than in the associated solution phase. Craig (1980) notes a specific example where lead pollution was detected in sediments but not in the associated solution phase.

Although sediments have largely been used to detect pollution sources they are also a valuable tool for detecting and determining the occurrence of natural levels of metals derived from country rocks. Förstner & Wittman (1979) emphasise that the fate of cations, derived from the chemical and physical degradation of host rock material, is controlled by a number of factors, such as atmospheric precipitation, water movement, soil movement, changes in redox and pH conditions, sorption processes, chemical complexation, precipitation and hydrolysis, and a variety of biological processes. The net result is that the metals are concentrated in sediments as one species or another.

The importance of lake-type environments in detecting pollution sources cannot be over-emphasised. If it is accepted that most potential pollutants accumulate in the fine fraction of the sediment, then, considering the nature of sedimentary processes, it would be fairly evident that impoundments are more appropriate foci for pollution studies than rivers (Ballinger & McKee, 1971). In high flow regimes, e.g. rivers, the flow rate generally exceeds the total load sedimentation rate, and it is likely that the particles will remain in suspension and be transported downstream. As the flow-rate subsides sedimentation will result, initially with the settling of the coarse-grained particles followed by the increasingly fine-grained particles. Flow rate may subside either due to periods of lower rainfall, e.g. seasonally controlled rainfall, or alternatively by coming into contact with large, stationary bodies of water, e.g. impoundments. It must be noted, though, that sediment deposited during low flow periods may be resuspended after periods of increased rainfall. Förstner & Wittman (1979) note that the size of grains transportable in suspension increases exponentially with the flow of the current. Therefore, resuspension is highly unlikely in deep aquatic sediments where currents are not as disruptive. The influence of wind driven currents and bioturbation has been suggested as causing sufficient turbulence to cause sediment winnowing, but it is unlikely that such effects will be significant in deep impoundments.

The result of sedimentation processes is that, when compared to rivers where shifts between the processes of erosion and deposition can take place within short intervals of time and space, impoundments exhibit a more continuous accumulation of sediment material. Associated with this would be a decrease in grain size from the input site to the central reaches of the impoundment, where one would expect an almost ubiquitous fine-grained material. It is the dominance of mostly

fine-grained material which suggests that a base line study of the Mgeni Catchment impoundments is necessary.

2.2 The study Area

2.2.1 Introduction

The Mgeni River has its source in an area known as the Umgeni Sponge, situated in the region of Spioenkop - some 32 km west of the Drakensberg Range, in the Kwazulu-Natal midlands. The river is separated from the Drakensberg by the adjacent catchments of the Umkomaas and Mooi Rivers, which both have higher sources. The approximate altitude of the source is 1830 m (Furness, 1974). The three rivers flow into the Indian Ocean, the Umkomaas to the south of Durban, the Mooi as a tributary of the Tugela to the north and the Mgeni at Durban (Fig. 2.1). The approximate size of the Mgeni catchment is 480 km^2. The major characteristic of the catchment is that it contains the two major population and industrial centres of Kwazulu-Natal, Durban and Pietermaritzburg. It is in the supply of water to these industrial centres that the decision to impound the river in a number of places was taken. A total of four impoundments have been constructed on the Mgeni River course, Midmar, Albert Falls, Nagle and Inanda and these are the impoundments which were studied. A fifth impoundment, Henley, was also chosen for this study. Henley is situated on the Msunduzi, the major tributary of the Mgeni (Fig. 2.1).

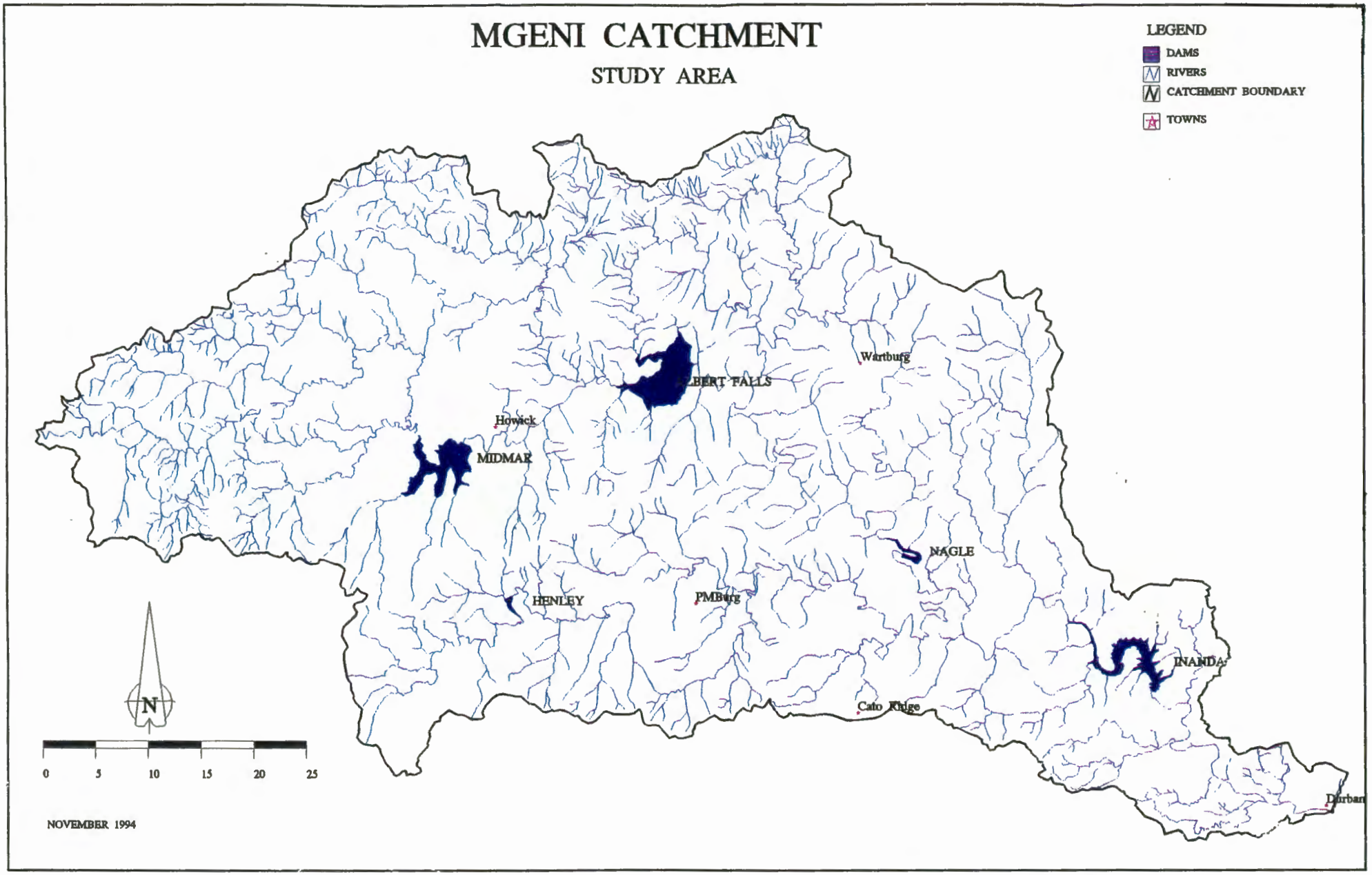


Figure 2.1 Location map of the five impoundments in the Mgeni Catchment

2.2.1 Descriptions of the impoundments

To meet the growing water demands of the Durban-Pietermaritzburg region it was realised in the early 1960's that the Mgeni River would have to be impounded in places along its course (Tollow, 1991). As a consequence, the Midmar Dam was constructed in the 1960's, followed by Albert Falls in the 1970's and finally by Inanda in the 1980's. Nagle had been completed in the 1950's, and Henley dam had been completed prior to that. Details of the nature of the impoundments are given in Table 2.1.

All of the impoundments studied are under the control of Umgeni Water, the Water Board of the area. Umgeni Water manages both the water quality and the water volume aspects of the impoundments.

2.2.3 Climate

2.2.3.1 Rainfall

The rainfall data for the impoundments appears in Table 2.2. It is evident from the data that rainfall is seasonal with the majority of the rain falling in the period October to March. This is reflected in the marked increase in average rainfall after September and the conspicuous decrease in rainfall after March, for all areas. It is also evident from the data that rainfall distribution is related closely to altitude, with those impoundments at higher altitudes experiencing noticeably higher rainfall figures. The exception to this trend is the Inanda site which has recorded significantly higher mean rainfall figures.

Table 2.1 Characteristics of Mgeni catchment impoundments

Impoundment	Location	Altititude (m amsl)	Use	Catchment Area (km^2)	Inflowing rivers with Catchment Area	Dam wall completed (year)	F.S.L. volume (m^3)	F.S.L. area (km^2)	F.S.L. max. depth (m)	F.S.L. mean depth (m)
Henley*a	29° 37' S 30° 15' E	931	Potable, yachting	219	Msunduzi 181 km^2 Msunduzane 30 km^2 Thenjane 8 km^2	1959	5.79×10^6	0.71	18.8	8.2
Nagle*b	29° 35' S 30° 37' E	404	Potable	883	Mgeni 875 km^2 Mposane 7 km^2	1950	24.67×10^6	1.62	38.1	15.2
Midmar*c	29° 30' S 30° 12' E	1046	Potable, recreation	928	Mgeni 803 km^2 Kwagqishi 61 km^2 Nguku 29 km^2 Umthinzima 19 km^2	1964	177.20×10^6	15.59	22.3	11.4
Albert Falls*d	29° 26' S 30° 25' E	656	River regulation, recreation	728	Mgeni 556 km^2 Nculwane 75 km^2 Doringspruit 41 km^2	1976	293.64×10^6	23.85	24.6	12.3
Inanda**	29° 40' S 30° 45' E	146	Potable	1322	Mgeni	1989	225×10^6	1440 ha	48.5	-

(amsl = above mean sea level and F.S.L. denotes Full Supply Level)

* Archibald *et al.* (1980a, b, c, d respectively)

** Tollow (1991)

Table 2.2 Mean yearly and monthly rainfall for Mgeni catchment impoundments

Impoundment	Data span (years)	Yearly mean (mm)	Monthly mean (mm)											
			Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Henley	43	938.2	151.4	123.1	114.3	54.3	23.7	10.0	11.2	32.3	61.2	98.1	121.6	136.1
Nagle	37	764.7	117.2	100.9	100.8	57.2	25.0	11.9	13.8	27.4	45.3	77.0	93.8	88.3
Midmar	52	990.7	152.2	139.4	116.1	65.1	35.3	18.2	18.0	34.4	66.2	97.4	117.5	131.0
Albert Falls	40	806.1	134.3	86.4	128.1	53.1	21.8	4.9	7.1	22.5	57.2	77.3	116.9	99.6
Inanda	42	1055.7	161.1	141.2	118.6	69.2	44.9	16.4	19.4	43.2	81.8	109.4	127.4	118.7

Source: Computing Centre for Water Research (University of Natal).

2.2.3.2 Temperature

Although no temperature data for the specific dams could be ascertained it is expected that the dams of the highlands would experience markedly lower average temperature than those dams situated in the lower reaches of the river. Donkin (1991) notes that the mean annual temperatures of the area are commonly between 13° C and 23° C, with the lower temperatures experienced in the highlands and the higher temperatures in the lowlands. As a consequence it would be anticipated that Inanda and Nagle Dams would have higher average winter and summer temperatures than the upstream dams. As higher temperatures are conducive to increased algal growth, the downstream dams are more likely to experience eutrophication problems.

2.2.4 Geology

Table 2.3 is an idealised stratigraphic column for the catchment area and depicts the percentage area that each stratigraphic unit occupies. The distribution of lithologies, with respect to individual impoundment catchment areas, is summarised in Appendix A. A brief description of the stratigraphic units follows. It should be noted that the discussion is regional and that lithological characteristics will vary within the area.

The lithology of the Beaufort Group is dominated by sedimentary units. The units have been described (Haughton, 1969) as alternating beds of sandstone, mudstone and shale. The sandstones are described as fine to medium grained quartzofeldspathic arenites. The mineralogy of the sandstone is dominated by quartz and feldspar, with the accessory minerals biotite, chlorite, muscovite, zircon and calcite (Haughton, 1969). The mudstones are described as greenish-grey, bluish, grey, or red (SACS, 1980). It is on a colour basis that the Beaufort mudstones are differentiated from the Ecca Group mudstones which are characteristically dark grey/black and are carbonaceous. Ecca Group shales have been noted (Haughton, 1969) to be rich in P. Grobler & Davies (1981) further note that sediments derived from the Karoo Sequence are rich in P.

Table 2.3 Idealised stratigraphic column of the Mgeni catchment

Stratigraphic unit			Symbol	Area covered (km^2)	Area covered (%)
Karoo Sequence	Beaufort Group	Tarkastad Subgroup	TRT	57	1.4
		Estcourt Subgroup	PE	94	2.3
		Adelaide Subgroup	PA	140	3.4
	Ecca Group	Vryheid Formation	PV & PVO	661	16.2
		Pietermaritzburg Formation	PP	656	16.1
	Dwyka Formation		C-PD	233	5.7
Natal Group			O-SN	524	12.8
Mafic Basement			BM	12	0.3
Granitic Basement			B	638	15.7
Karoo Dolerite			JD	913	22.4

The sediments of the Ecca Group comprise more than 30% of the catchment area, therefore, their significance as a potential source of P for the impoundments should not be discounted.

Underlying the Ecca Group are sediments of the Dwyka Formation. In the Mgeni catchment the Dwyka Formation is dominated by tillite. The tillite is a blue-green coloured rock (King & Maud, 1964) in fresh surface, which weathers to a yellow-brown coloured rock. By definition tillite contains clasts set within a fine grained rock flour. X-ray diffraction work carried out for George, Orr and Associates (1983) on the rock matrix yielded the following results: quartz (45-65%), plagioclase (23-35%), orthoclase (8-12%), and chlorite (2-5%). The clasts in the rock have variable diameters, ranging from 1 cm to 1 m, and variable composition. Hounsome (1993) recognised the presence of gneiss, granite, sandstone, quartzite and chert. Sandstone and chert are the most abundant inclusions.

The dominance of sandstone clasts in the Dwyka glacial sediments is not surprising considering that the tillite is underlain by sandstone of the Natal Group. Broadly defined, the Natal Group sandstone is a medium to coarse grain quartzofeldspathic rock. The rock is most often maroon in colour, the result of weathering; fresh surfaces of the rock are cream coloured (Hounsome, 1993). Quartz, K-feldspar, plagioclase, hematite and muscovite, in different modal proportions, have been recognised in the sandstone, while the results of weathering - kaolinite and goethite - have also been described (Roberts, 1981). Visser (1974) states that the source area of the sandstone most probably consisted of granite-gneiss from the Basement Complex.

The Basement Complex of the Mgeni catchment is dominated by the Mgeni Megacrystic Granite Complex (Kerr *et al.*, 1988a). The majority of the rocks of the area comprise K-feldspar megacrysts with minor phases of quartz and plagioclase, set in a matrix of feldspars, quartz, plagioclase and mafic minerals (Kerr *et al.*, 1988b). Mafic minerals described from the area include biotite, hornblende, clinopyroxene, orthopyroxene and garnet (Kerr *et al.*, 1988a and 1988b). Allanite, zircon and apatite have also been described. Kerr *et al.* (1988b) describe the geochemistry of the granites as being rich in Fe, K, Ti, P, Nb, Zr, Y, and Zn while having low concentrations of Ca, Mg, and Al.

The most wide-spread lithology of the area is the Karoo dolerites occurring extensively as dykes and sills. Dolerite intrusions are resistant to weathering and result in hills and ridges which are prevalent in the Natal midlands. Furness (1974) notes that sills provide good dam sites e.g. Midmar Dam. Mineralogically, the dolerite is composed of Ca-, or Na-plagioclase, depending on the thickness of the sill; pyroxenes, which are often Fe rich, and olivine (Truswell, 1977). The resistance of the rock to erosion would suggest that these minerals are unlikely to provide ionic nutrients to the impoundments.

2.2.5 Soil types

Donkin (1991) describes the soils of the area as "mature soils which are generally freely drained, acid, with topsoils high in organic carbon". Donkin (1991) also noted that soils derived from a doleritic parent material are commonly red clay soils, while the Karoo sediments are likely to give rise to yellow-brown clay soils. The Natal Group was noticed to give rise to dark-brown soils, often moist and clayey in nature (Donkin, 1991).

A Land-type map, produced by the Department of Agricultural Development in conjunction with the Soil and Irrigation Research Institute in 1992, indicates the ubiquitous presence of dystrophic or mesotrophic soils throughout the area. Dystrophic and mesotrophic soils are highly leached such that the presence of the exchangeable cations, Ca, Mg, K, and Na, is often very low (Soil Classification Working Group, 1991). Dystrophic and mesotrophic soils develop after intense weathering.

2.2.6 Land use

Given the size of the catchment area it is difficult to discuss the land use in great detail. Rather, a few salient aspects, which indicate possible sources of nutrients to the impoundments, will be discussed. Details of percentage land-use types for each catchment area are presented in Appendix A.

Of particular importance, as a diffuse source of P, are the Black Transitional areas (BTA) of high density informal settlement. Although these do not make up extensive areas of the catchment their influence should not be ignored. The BTA's are largely unsanitised and, therefore, contribute faecal derived P to the impoundments. A further source of P from these areas could be washing detergents.

The presence of formal farmlands in the catchment area is possibly the most important source of P. Furness (1974) categorised farming activity into three groupings:

(i) Intensive arable farming, which depends on arable land. Cash crops, pigs, and poultry are likely to be farmed. Cash crops in the Mgeni catchment include sugar cane, maize, and industrial forestry. Favourable climatic conditions in the Mgeni catchment suit this category of farming.
(ii) Semi-intensive farming, which depends on natural grassland but may be supplemented by production from arable land and intensive pastures.
(iii) Extensive farming which depends wholly on production from natural grassland. Beef and sheep are most commonly farmed.

Of the three groupings, it is intensive fertilised arable farming which is likely to provide the greatest contribution of P to the impoundments.

There are limited point sources in the catchment. Only Inanda and Midmar are likely to be influenced by point source P. Industrial and urban areas, e.g. Pietermaritzburg, and the Darvill waste water works, situated on the Umsunduze River, are the major P point source contributors.

The majority of the population of the catchment is located around the major metropolitan areas, with the lowest population density areas found in the highlands. It is interesting to note that a relatively high population density exists in the Valley of a Thousand Hills around the Inanda Dam, an area demarcated as a BTA.

The presence of industry, particularly in the urban areas, is a further potential source of pollution to the area.

2.2.7 Conclusion

The terrain of the Mgeni catchment area is diverse. As a consequence of this diversity it is expected that the sediment from the five impoundments will have distinctly different properties. Based on the fact that the properties are likely to be different it would further be expected that the P sorption characteristics of sediments taken from each dam are likely to be different.

To determine which properties differ between the sediments of each impoundment and to ascertain whether they have a significant control on the P sorption capacity, it was necessary to take sediment samples from each impoundment for analysis.

2.3 Materials and Methods

2.3.1 Sediment sampling and preparation

2.3.1.1 Sampling procedure

Sediment samples were taken from each impoundment, mostly at sites which coincide with the water quality sampling sites established by Umgeni Water. Certain impoundments had more sampling sites than others (Table 2.4).

Table 2.4 Impoundment sampling points and sample numbers

Impoundment	Sample number	Description of sampling point
Henley	H	Outlet, near the dam wall
Nagle	N1	Outlet, near the dam wall
	N2	Central basin, point of water abstraction
Midmar	M1	Outlet, near the dam wall
	M2	Inlet (Umthinzima tributary)
	M3*	Inlet (Mgeni)
Albert Falls	AF	Outlet, near the dam wall
Inanda	I1*	Inlet (Mgeni)
	I2	Central dam reaches
	I3	Outlet, near the dam wall.

Those samples marked (*) were not taken at sites which coincide with Umgeni Water sampling points. These sites were chosen because it was felt that they better represented the intended area than the Umgeni Water sampling sites.

Sampling commenced on the 6th August 1994 and continued for about one-and-a-half weeks. A different dam's sediments were sampled each day. Samples were taken from a boat using a van Veen grab sampler which is a standard device for sampling reservoir sediments. The grab was lowered under tension to the sediment surface. At the surface, the tension was released causing the arms of the grab to close and to trap the sediment. The grab and sediment were then lifted onto the boat where the grab was opened and the sediment slurry allowed to flow into a pre-washed bucket. The slurry was then poured from the bucket into 1 litre plastic containers which were then sealed. The containers were labelled and pre-washed to avoid contamination, and covered to limit the effects of sunshine. Six van Veen samples were taken at each site and these were compounded to make one representative sample.

The ideal sampling method for P sorption work is a sediment coring technique, whereby it would be possible to differentiate the different sorption characteristics of different horizons. Sediment coring is, however, a more time consuming process than grab sampling. Most P transfer reactions

take place at the sediment/water interface, therefore, the van Veen grab, which samples the upper layer of sediment, was considered to be suitable for the present study.

2.3.1.2 Drying procedure

The preparation of the sediment samples prior to laboratory analysis required them to be dried. Samples were spread onto plastic trays and air-dried. Twinch (1987) suggested that the air-drying of samples could possibly alter the chemical and physical characteristics of sediments to be analysed for their P exchange characteristics. Twinch (1987) further goes on to suggest that the standard procedures for preparing samples for phosphorus analysis, including oven-drying, partial drying, freezing and freeze-drying, could also be unsuitable. Although Twinch (1987) found significant statistical differences in the P sorption characteristics of wet and dried sediments, his results contradict those found by other workers who he cited as having reported no P sorption differences between wet and dry sediment samples. Air drying was selected in preference to oven drying.

Sub-samples of the Inanda sediments were retained in their wet, reduced form in sealed plastic containers.

2.3.1.3 Sample preparation

Prior to analysis the samples were gently ground using a mortar and pestle to pass through a 2mm screen, and stored in 1 l plastic containers.

2.3.2 Sediment Analyses

A more detailed description of each of the following methods is presented in Appendix B.

2.3.2.1 Bulk elemental concentrations

The major and trace elemental constituents of the dry sediment samples were analysed using X-ray fluorescence spectroscopy (XRFS) techniques. Samples were dried and then crushed to a fine powder in a swingmill using a carbon steel vessel. Powder briquettes and fusion discs were made for trace and major element analysis respectively. Major elemental results were expressed as oxide percentages and the trace element results as parts per million (ppm).

2.3.2.2 Clay mineral identification

The clay minerals were identified by X-ray diffractometry (XRD) techniques, after the clay size (< 2 μm) fraction had been separated from the remaining particle sizes. The separated clay slurry was pipetted onto a frosted glass slide and allowed to dry. XRD scans were carried out from 4-30° 2θ using CuKα radiation.

2.3.2.3 Organic carbon

Organic carbon was determined using the standard Walkley-Black technique (The Non-Affiliated Soil Analysis Work Committee, 1990). The method consists of oxidising the organic material in soil with a treatment of potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid.

2.3.2.4 Sediment pH in 1M KCl

The sediment pH of the samples was determined in a suspension of 10 g wet sediment, in its original (reduced) state, equilibrated for 1 hour with 25 cm^3 1M KCl, using a Crison Micro pH 2001 meter fitted with a combination glass electrode. Measurements were taken every 24 hours to determine the influence of oxidation on the sediment pH condition.

2.3.2.5 P fractionation

Sequential fractionation of the sediment P was carried out using the technique described by Hieltjes & Lijklema (1980). Sediment P fractionation was carried out after sequential extraction with 1M NH_4Cl, 0.1M NaOH and 0.5M HCl. The extractants were analysed for P using the Murphy & Riley (1962) colorimetric method.

2.3.2.6 Colorimetric analysis of P

All P analyses in solution were carried out using the Murphy & Riley (1962) molybdate-blue colorimetric method.

2.3.2.7 Particle size distribution (PSD)

Particle size distribution was determined using the standard sedimentation technique based on the pipette method (The Non-Affiliated Soil Analysis Work Committee, 1990), followed by screening of the dried sand fraction. Sediment samples were pre-treated with hydrogen peroxide, citrate-bicarbonate, and sodium dithionite. Dispersion was ensured by treatment of the sample with Calgon solution and an overnight shaking period. The particle size results are expressed as sand, silt and clay fractions.

2.3.2.8 Specific surface area

The particle surface areas of the Inanda samples were determined using a Micrometrics ASAP 2000 instrument, by the BET method with N2 as the absorbing gas.

2.4 Results and discussion

The details of the analytical results are listed in Appendix B, along with any data manipulation that was required in the processing of those results.

2.4.1 Particle size distribution

The sediments sampled are dominated by a clay-sized material (< 2 μm). The predominance of this sized material may be related to one of two features. The first is the relationship between the physical nature of the dams and sedimentology; given the fact that the dams are deep and generally free of currents, it would be expected that the clay fraction would dominate. A second feature, which could be considered, is that samples were taken at the end of the dry season when flow-regimes are correspondingly low. This would seasonally bias the sediment size fraction in favour of a more clayey material, particularly in areas where grain size is influenced by currents - i.e. inflow sites. If one considers Figure 2.4 it is evident that the samples taken at inflow sites, samples M3 and I1 (marked with an asterisk) already trend towards being more silty or sandy than the other samples taken from the same impoundments. It is envisaged that while there might be an increase shift towards siltier/sandier material at the inflow sites, that shift would not affect the majority of the samples.

The nature of the material and the expected association of the fine-grained material with potential pollutants definitely suggests that the sediments sampled are ideal for the study of anthropogenic and naturally derived pollutants in the impoundments.

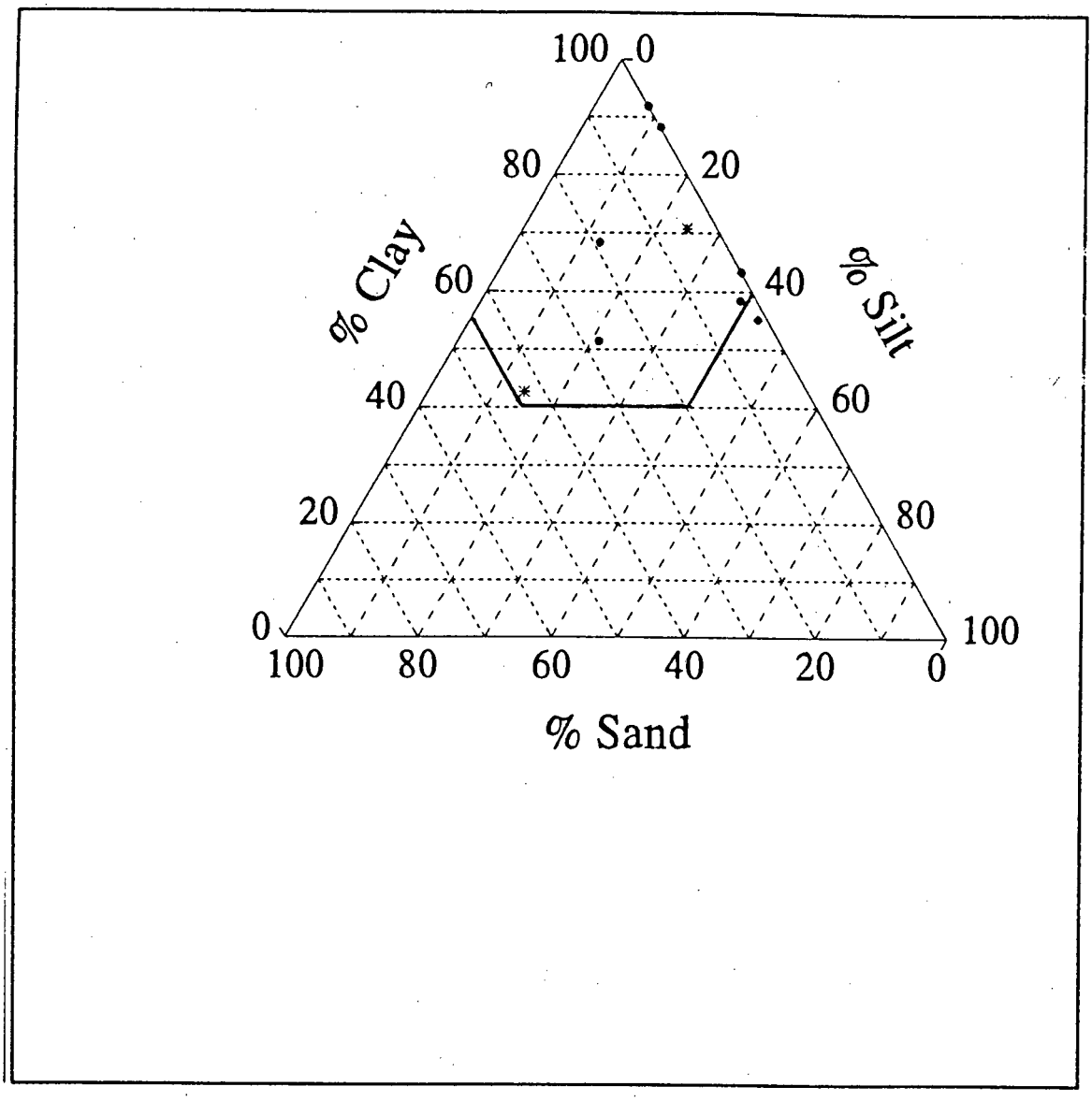


Figure 2.4 Particle size distribution plot for the Mgeni Catchment sediments. The circles indicate samples taken in the central reaches of the impoundments and the asterisks are those samples taken at the inlet sites of the dams. The area denoted by the solid line and in which most of the samples fall corresponds to the clay textural class (according to the Soil Classification Working Group, 1991)

The almost ubiquitous fine-grained nature of the sediments perhaps makes interpretation of the data far easier. In cases where the fine fraction of the sediment is less dominant than the coarse-grained material the latter effectively "drowns-out" evidence of possible contamination or enrichment by pollutants. A number of methods for the avoidance of grain-size effects have been proposed but it is envisaged that these methods need not be invoked for the dominantly fine-grained material of the Mgeni impoundments.

2.4.2 Elemental concentrations

Any discussion about the background levels of particular elements in aquatic sediments, needs to take into consideration the parent material from which the sediment was derived. If a comparison is made between the analysed trace element concentrations (Table 2.5) and the global average concentrations for rock types, corresponding to common parent materials in the catchment area (Table 2.6), then a few trends become apparent and a few interesting observations can be made. Comparisons have been drawn using global averages in the absence of relevant local figures. Donkin (1991) presented XRFS analyses for soils of the area but these are incomplete for comparison with the present results. Trace element concentrations were chosen to be discussed in more detail than major elements because of their greater potential significance as pollutants.

With the exception of a few samples, in relation to particular elements, it would appear that the sediments contain trace element concentrations that are broadly higher than the average geologic materials present in the catchment. There are a few exceptions to this general case.

Of the elements analysed it would appear as if nickel and vanadium are the only ones which do not seem to show any enrichment in any of the samples. On the other hand the concentration of lead, cobalt and chromium seem to be enriched in all of the samples. This wide-spread "enrichment" should be treated with caution as it the may be the result of a regional phenomenon. In certain samples, distinctly higher concentrations of chromium, zinc, molybdenum, manganese, and copper are recognised.

Table 2.5 Results of XRFS analyses for trace elements (mg/kg) in Mgeni sediments

	M1	M2	M3	I1	I2	I3	N1	N2	AF	H
Mo	1.1	.7	<.5	1.9	2.6	2.4	1.6	1.4	.9	1.1
Nb	20	22	15	25	26	25	21	19	20	19
Zr	239	316	479	272	136	128	170	266	382	227
Y	33	33	27	60	66	65	43	37	35	38
Sr	39	40	27	84	62	57	59	61	61	45
U	4.1	3.8	1.9	3.0	3.3	3.3	3.8	2.4	3.9	4.4
Rb	102	88	28	119	129	132	114	100	84	103
Th	15	17	9.7	25	28	27	21	18	16	17
Pb	30	29	19	37	39	37	34	30	26	28
Zn	86	75	51	103	120	125	88	74	72	100
Cu	53	48	38	31	38	40	50	63	37	54
Ni	67	53	65	43	50	50	64	53	53	58
Co	36	35	32	24	26	34	36	31	26	33
Mn	741	773	798	842	1149	6436	1945	1651	970	715
Cr	179	162	212	126	134	119	175	150	188	163
V	173	144	159	115	143	146	168	150	143	164

Table 2.6 Average global concentrations (mg/kg) of trace elements in selected rock types (from Förstner & Wittmann, 1979; Sposito, 1989)

Trace element	Average granite	Average shale	Average sandstone	Enrichment factor*
Mo	1.0	2.6	0.2	0.65
Pb	15	20	7	1.40
Zn	60	95	16	0.80
Cu	30	45	15	0.50
Ni	15	68	2	0.24
Co	7	19	0.3	0.46
Mn	540	850	390	0.58
Cr	22	90	35	0.54
V	88	130	20	0.50

(*Calculated as soil content/crustal content, where soil content concentrations were derived from Sposito (1989))

In a geochemical context, simply recognising that certain samples appear to have elevated concentrations of particular elements is insufficient because those elevations may be the result of elemental accumulations. In the light of possible accumulations a correlation matrix was constructed in an attempt to associate certain variables. It was considered that certain variables, namely Al_2O_3, Fe_2O_3, clay, organic carbon (O.C.) and loss on ignition (LOI) (Table 2.7), might have a significant influence on the distribution of metals in sediments and would be most likely to correlate with trace metal distribution. LOI has been included together with the other variables because ignition at 550° C drives off all organic volatiles, and a loss of mass after such ignition is considered to be a measure of organic content (Keulder, 1982). While this may be the case it is envisaged that high temperature ignition will also expel any water which is structurally bound in clay particles. In any event, LOI and O.C. should, to a large extent, reflect the organic matter content.

The correlation matrix presented (Table 2.8) indicates some interesting phenomena. Highly significant correlations are evident between Al_2O_3 and Fe_2O_3, clay, LOI, P_2O_5, and Pb; between Fe_2O_3 and clay, LOI, P_2O_5, and Zn; between clay and LOI, P_2O_5, Mo, and Pb; and between LOI and P_2O_5, Mo, and Pb.

It was expected that O.C. would correlate with Al_2O_3, Fe_2O_3, or clay concentration since between 52 and 98% of O.C. is associated with clay minerals and related oxides in sediments (Paul & Huang, 1980). No such correlation was realised suggesting that O.C. is not significant in determining the characteristics of the sediments.

The fact that the Al_2O_3, Fe_2O_3 and clay variables correlate so strongly is a reflection of the chemical and mineralogical composition of the clay fraction of the sediments. The clay diffractograms (Figure 2.5) indicate the presence of 2:1 layer silicates, kaolinite, gibbsite, goethite, and quartz. The 2:1 layer silicates are represented by the expanded 2:1 layer minerals, e.g. smectite, vermiculite, or chlorite, and the collapsed 2:1 layer silicates in the form of mica. Differentiation of the expanded minerals by glyceration of the glass slide mounts or by sequential heating was not carried out.

Table 2.7 Results of XRFS analysis for major elements

wt %	M1	M2	M3	I1	I2	I3	N1	N2	AF	H
SiO_2	54.26	63.07	67.00	51.86	46.91	47.84	51.77	58.83	63.83	53.04
TiO_2	1.16	1.27	1.82	1.11	1.13	1.05	1.14	1.06	1.15	1.04
Al_2O_3	19.04	13.92	11.75	19.49	22.35	21.24	20.95	16.67	15.26	20.24
Fe_2O_3	9.56	7.32	8.07	7.75	10.03	11.28	10.11	8.57	7.23	8.86
MnO	.09	.09	.09	.10	.14	.79	.23	.19	.11	.09
MgO	.70	.54	.34	.83	.86	.85	.83	.69	.59	.68
CaO	.30	.34	.26	.75	.41	.46	.37	.40	.32	.29
Na_2O	.12	.17	.09	.42	.33	.34	.24	.28	.30	.17
K_2O	1.32	1.13	.35	2.10	1.75	1.79	1.60	1.53	1.47	1.61
P_2O_5	.18	.14	.14	.23	.27	.31	.21	.19	.14	.16
H_2O^-	3.34	2.07	2.27	2.29	2.65	2.40	2.11	.92	1.98	2.28
LOI	10.10	9.35	7.48	13.20	13.15	13.32	11.30	9.84	7.35	11.20
Total	100.17	99.40	99.65	100.14	99.97	101.66	100.86	99.15	99.72	
Organic C (%)	1.90	2.77	1.52	3.53	2.44	2.40	1.79	1.62	1.03	2.17
Clay (%)	63.33	55.17	42.72	70.75	88.24	91.89	88.24	68.40	51.48	58.43

Table 2.8 Correlation matrix associating trace element concentrations with possible controlling variables

Al_2O_3														
Fe_2O_3	.76*													
O.C.	.36	.03												
LOI	.87**	.64*	.71*											
Clay	.85**	.81**	.33	.83**										
P_2O_5	.77**	.78**	.43	.87**	.90**									
Mo	.76*	.76*	.40	.84**	.89**	.99**								
Pb	.85**	.56	.61	.91**	.90**	.85**	.84**							
Zn	.61	.77**	-.11	.42	.60	.53	.59	.42						
Cu	.02	.13	-.33	-.16	-.03	-.27	-.27	-.17	.23					
Ni	-.23	.15	-.60	-.50	-.30	-.46	-.51	-.57	.05	.43				
Co	-.05	.37	-.21	-.14	.02	-.15	-.17	-.23	.32	.62	.70*			
Mn	.38	.07	.07	.45	.62	.73*	.77**	.41	.55	-.09	-.23	.23		
Cr	-.67**	-.41	-.71*	-.88**	-.72*	-.81**	-.83**	-.88**	-.35	.14	.78**	.29	-.51	
V	-.00	.36	-.61	-.33	-.10	-29	-.31	-.40	.38	.63	.92**	.78**	-.05	.58
	Al_2O_3	Fe_2O_3	O.C.	LOI	Clay	P_2O_5	Mo	Pb	Zn	Cu	Ni	Co	Mn	Cr

(where: n=10, * = $p<0.05$, ** = $p<0.01$)

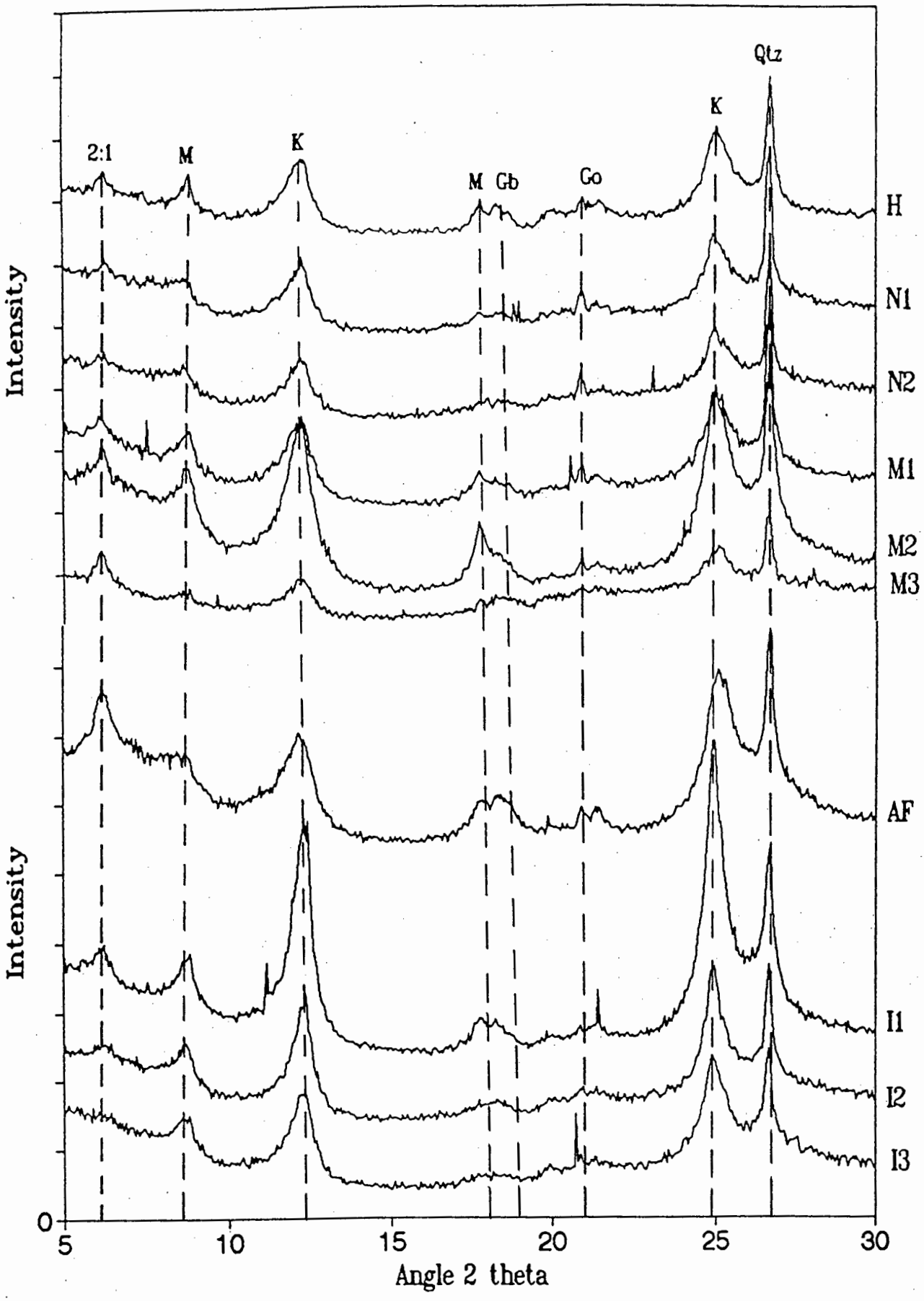


Figure 2.5 Clay mineral diffractogram for Mgeni Catchment sediments (where: 2:1 = expanded aluminosilicates, M = mica, K = kaolinite, Gb = gibbsite, Go = goethite, Qtz = quartz)

It is concluded that the presence of kaolinite ($[Si_4]Al_4O_{10}(OH)_8.nH_2O$), gibbsite ($Al(OH)_3$), and goethite (FeOOH) in the clay fraction account for the strong correlations observed. The significance of the particular mineralogy observed in the samples will be discussed in more detail later.

The correlations between Al_2O_3, Fe_2O_3, and clay with Pb, Zn, and Mo, respectively, are of particular interest in relation to the elevated concentrations observed for these trace elements. Specific attention is drawn to samples I2 and I3, which contain high concentrations of Mo, Zn, and Pb, as well as high concentrations of clay, Al_2O_3 and Fe_2O_3. This would seem to suggest that, while concentrations of the metals appear to be elevated, these enhancements are not necessarily due to contamination, but rather to their association with clay minerals. Although it was initially suggested that grain size effects were unlikely to be influential given the clayey material sampled, it is the high content of clay material which seems to have led to high elemental concentrations.

The relationship between concentrations of P_2O_5 (total P) and those of a number of other parameters is also significant and will be discussed later.

The correlations between Pb, Zn and Mo and the chosen controlling parameters (Al_2O_3, Fe_2O_3 and clay concentrations) are consistent with those which might be expected for sedimentary environments (Diamond *et al.*, 1990). A limitation of the correlation analysis is that it give no indication about the speciation of the metals in solution and some understanding needs to be gained about possible metal speciation. This may be achieved by using computer speciation techniques.

Four types of metal associations are present in aquatic sediments, and these are: (i) adsorptive bonding, (ii) co-precipitation, (iii) organic complexation, and (iv) incorporation into crystalline minerals. Sposito (1989) refines the processes by noting that trace metal associations with soil minerals correspond to a phenomenon which he calls co-precipitation. Sposito (1989) notes three modes of co-precipitation, namely:

1. inclusion - occurring where the host material and trace element exist as morphologically distinct solids, with no affinity between the materials;

2. adsorption - occurring when a limited structural compatibility results in a homogeneous mixture of two elements;
3. solid-solution formation - resulting from a high structural compatibility between the species resulting in a major element in the host material being replaced uniformly by the trace element.

Sposito (1989) further goes on to note which trace elements are most likely to be co-precipitated with which minerals (Table 2.9).

Table 2.9 Trace elements likely to be co-precipitated with soil minerals and soil organic matter (from Sposito, 1989)

Mineral species	Trace element
Fe and Al oxides	B, P, V, Mn, Ni, Cu, Zn, Mo, As, Se
Mn oxides	P, Fe, Co, Ni, Zn, Mo, As, Se, Pb
Ca carbonates	P, V, Mn, Fe, Co, Cd
Illites	B, V, Ni, Co, Cr, Cu, Zn, Mo, As, Se, Pb
Smectites	B, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb
Vermiculites	Ti, Mn, Fe
Organic matter	Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb

It is not possible from the limited experimental data to conclusively assume any particular mode of co-precipitation. If it is assumed, however, that adsorption is the most likely to have occurred, then the essential process of adsorption, of metal ions, is cation exchange. The cation exchange capacity of the sediment was not determined, however, it is envisaged that pH (KCl) could be used as an indicator of ion exchange. A major contribution to exchangeable acidity is made by the readily exchangeable forms of Al (III): Al^{3+}, $AlOH^{2+}$, and $Al(OH)^{2+}$ (Sposito, 1989). The measured acidity in a KCl solution extract results when proton release from Al (III) species takes place after Al (III) has been replaced by K^{+}. The importance of Al (III) as an acidic cation is in that the pH of a solution is virtually proportional to the activity of Al^{3+}. As pH increases there is a dominance of the anionic hydroxide Al species, while the cationic species are dominant at low pH conditions.

The assumption that Al has a noticeable influence on the cation exchange capacity of the sediment is based on the fact that the sediment phases are primarily controlled by the distribution of Al. Sposito (1989) notes that the dominant phases that control Al^{3+} in soils, and therefore in sediments, are gibbsite, kaolinite, beidellite and vermiculite. As two and possibly three of the four mineral phases have been recognised in the sediments, it is suggested that the activity of Al^{3+} is most significant in influencing soil acidity. It is, therefore, reasonable to assume that the net surface charge of the sediments is negative, implying cation rather than anion exchange.

Although it has been suggested that cation exchange of Al^{3+} in clay minerals is the most likely form of co-precipitation, it is further expected that the oxides, hydroxides, and oxyhydroxides of Al and Fe also play a significant role as potential sinks of metals in impoundments. These oxides readily sorb, or co-precipitate, cations and anions to the extent that even a low concentration of the species has a controlling influence on metal distribution in aquatic sediments (Sparks, 1986). This is especially true for amorphous oxides which often result in environments where organic matter content is high, therefore partially explaining the correlation between LOI (organic matter) and some metals. Hydroxides occurring as coatings on clay or silt particles have a significant role in sorption reactions (Förstner & Wittman, 1979). The identification of such coatings would only have been possible using electron microscopy techniques.

Although the correlation between organic matter and metals has been linked to its influence on mineral crystallinity, the important role of organic functional groups should not be neglected. It has been suggested that organic matter has a significantly greater influence on cation exchange than clay minerals.

2.4.3 Sediment pH

If the metals are present in the sediment as adsorbed cations it suggests that the solubility of the species is closely linked to pH. A drop in pH may potentially result in the release of cations into solution (Sposito, 1984). Such reactions take place when the proton activity is sufficient to displace the sorbed species.

One of the major controls of pH in sediments is redox potential. If one considers the example of goethite, one of the mineral phases suggested to control cation distribution, then the redox reaction would be represented by the following equation:

$$Fe^{2+}(aq) + 2H_2O(l) = FeOOH + 3H^+ + e^-$$

It is evident that oxidising the ferrous iron will result in pH decrease. The pH readings taken over a period of five days, during which time the sediments oxidised, seem to confirm this statement. Figure 2.6 shows the decrease in pH as the samples oxidised for seven of the ten samples. The remaining three samples (H, M3 and AF) showed either no change or an increase in pH over time. It is possible that these samples were in a semi-oxidised state prior to experimentation and, therefore, oxidation was limited causing a negligible change in pH conditions.

If the influence of pH were accepted, it is conceivable that seasonal changes, resulting in potential lake turn-over, may result in the potential oxidation of the sediment. Such oxidation, through its influence on pH, could result in the release of cations into solution. A drop in redox, not associated with pH changes, could further result in a release of sorbed cations when Fe or Al hydroxides are partially or completely dissolved, allowing the metals to be released (Furumai & Ohgaki, 1989).

2.4.4 Geochemical anomalies

While the explanations of metal associations with clay, Al_2O_3, Fe_2O_3, and LOI may explain some of the apparent metal elevations, it is fairly evident that certain samples are sufficiently different from others to suggest abnormal conditions. Of particular note are the high concentration of Mn in sample I3 and the Cr concentration in M3 (Table 2.5).

The extremely high concentration of Mn in sample I3 definitely suggests extraordinary environmental conditions. This anomaly may be due to differential sedimentation within the dam, with Mn oxides being concentrated in the fine clay fraction. With the inclusion of I3 in the correlation analysis, Mn did not correlate with Al_2O_3, Fe_2O_3, clay or LOI. When I3 was removed and correlation was carried out it was shown that Mn correlates with clay ($r = 0.70$) at 95 %

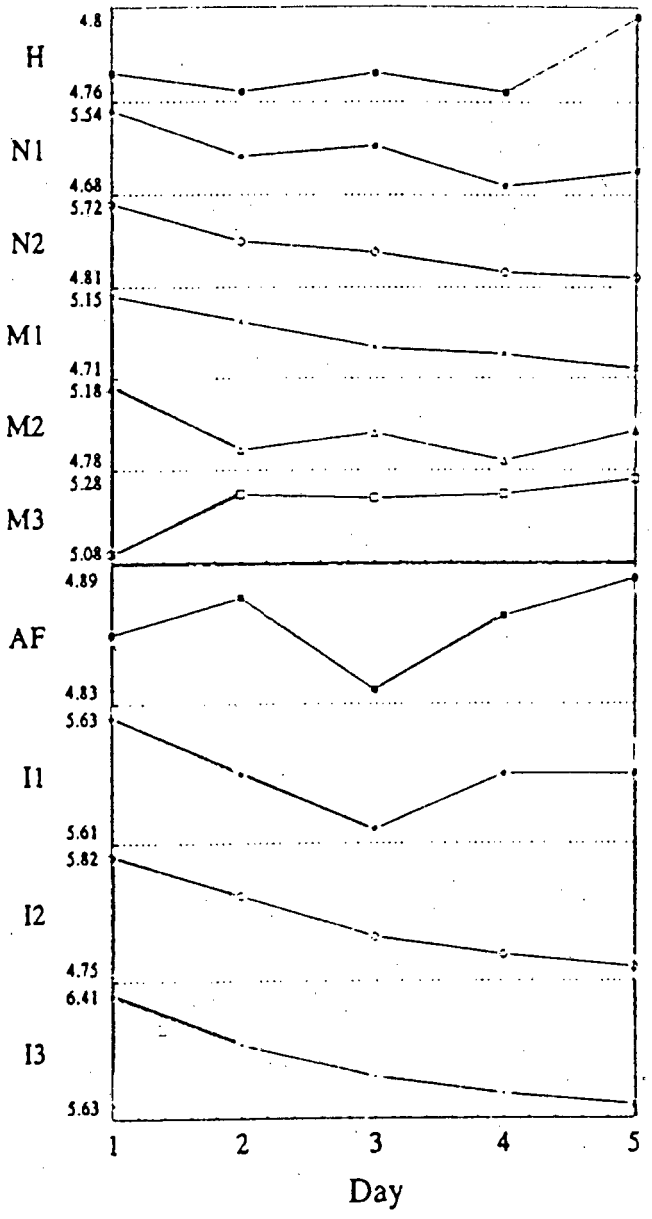


Figure 2.6 pH measurements in KCl taken over 5 days. Note particularly the decrease in pH associated with samples N1, N2, M1, I2, I3.

confidence level. The fact that the Mn concentration does not correlate with the clay content in the sediments may be due to the fact that the particle size distribution does not distinguish between the bulk clay fraction and the finer clay within this fraction.

The elevated concentration of Cr in sample M3 is also noteworthy. While there is a negative correlation between Cr and clay, this correlation does not necessarily account for slightly higher Cr concentrations. Cr has been especially pointed out because it is an especially toxic element in its oxidised (Cr (VI)) state. Fortunately Cr occurring within sediments is in a reduced form and is generally not toxic. While the Cr levels are not especially high it would be worthwhile considering potential diffuse and point sources of the element in the upstream areas of the Mgeni and Lions Rivers.

2.4.5 The distribution of P

There is a strong correlation of P_2O_5 concentration with Al_2O_3, Fe_2O_3, clay, LOI, and Pb (Table 2.8) indicating that P distribution is similar to that of the trace metals.

Although P sorption and distribution in sediments will be dealt with in the following chapter, one particular aspect of P sorption that is worth mentioning is that if P were associated with Al_2O_3, Fe_2O_3 and clay mineral phases, then the bonds are likely to be strong (Froelich, 1988) and will not readily relinquish their sorbed species. If this were the case then it would be unlikely that readily exchangeable P would correlate with Al_2O_3, Fe_2O_3, and clay. The correlation co-efficients presented in Table 2.10 seem to indicate that this theory holds true.

Table 2.10 Correlation co-efficients of labile P (NH_4Cl extractable) with potential controlling parameters

	Al_2O_3	Fe_2O_3	Clay	LOI	O.C.	MnO	CaO	P_2O_5
Labile P	.33	.54	.55	.47	.29	.88**	.39	.67*

(where: ** = $p<0.01$, and * = $p<0.05$)

It is evident that labile P correlates only with the sediment MnO content. According to Boyle & Lindsay (1986), Mn phosphates are likely to be more stable than Al or Fe complexes. Interestingly if the Mn-rich sample (I3) is removed from the regression analysis, the correlation of labile P with MnO is no longer significant (r=0.47). This suggests that possible correlation between Mn and labile P contents implied by the data should be viewed with caution.

2.4.6 The significance of sediment texture as an index of elemental abundance

Most of the preceding discussion has examined the data from the point of view of the clay fraction. Such an outlook was taken because reactive colloidal constituents (clay minerals, oxides and organic matter) can be expected to play the most significant role in the general speciation of elements in sediments. It should, however, be pointed out that the coarse grained material in the sediment will also have relevant geochemical associations. A correlation matrix was constructed (Table 2.11) relating the sand fraction to a number of variables and some noteworthy trends were recognised.

Table 2.11 Correlation matrix of sand with relevant variables

SiO_2							
TiO_2	.66*						
Zr	.94**	.75*					
Sand	.79**	.72*	.86**				
Silt	.24	-.08	.20	-.27			
Clay	-.88**	-.58	-.91**	-.68*	-.52		
O.C.	-.48	-.25	-.37	-.59	.25	.33	
P_2O_5	-.86**	-.45	-.79**	-.53	-.57	.90**	.43
	SiO_2	TiO_2	Zr	Sand	Silt	Clay	O.C.

(Where: n=10, * = $p < 0.05$, ** = $p < 0.01$)

It is evident that sand correlates strongly with SiO_2, TiO_2, and Zr, while the negative correlation with the clay content was to be expected. The correlation of sand with SiO_2 was expected because

the sand fraction in most sediments is dominated by the presence of quartz. The clay fraction contains quartz, but not necessarily as a dominant constituent.

Weathering of the rocks of the area is likely to be the source of the Zr and Ti in the impoundments, especially since the rocks contain the minerals zirconium and rutile/ilmenite. These minerals have relatively high specific gravities which often results in them concentrating in the sand fraction, regardless of their particle size.

It would appear then that the distribution of trace elements is closely related to the clay and sand size fractions in the sediments, depending on their relative properties. While the importance of the sand fraction is acknowledged, it is the clay fraction which plays a far greater role because of its importance to trace element distribution.

The clay minerals identified in Figure 2.5 indicate that the soils in the Mgeni Catchment are in intermediate to advanced stages of weathering, as reflected by the presence of the leached minerals, kaolinite, gibbsite and goethite. Donkin (1991) recognises that in high rainfall, humid regions, such as Natal, chemical weathering is the dominant process. Weathering of materials in the catchment falls beyond the scope of this study and it is sufficient to mention that the soils of the area are highly susceptible to conditions which favour chemical weathering and the leaching of ions from the soil.

It is, therefore, relevant to mention that the particular interactions which take place between the clay minerals and the metal species in solution are the result primarily of the properties of the catchment leading to particularly high degrees of weathering of related minerals.

There are a number of indices which could be used to indicate the degree of weathering in soils and sediments. Two such indices (SiO_2/R_2O_3 and SiO_2/Al_2O_3) have been calculated for the Mgeni catchment sediments and the results are presented in Table 2.12. R_2O_3 represents the sesquioxides ($Al_2O_3 + Fe_2O_3$), all calculations were based on molar ratios.

Table 2.12 Weathering indices for Mgeni catchment sediments

Sample	SiO_2/R_2O_3	SiO_2/Al_2O_3
H	3.47	2.62
N1	3.20	2.47
N2	4.51	3.53
M1	3.66	2.85
M2	5.75	4.53
M3	6.73	5.70
AF	5.45	4.18
I1	3.60	2.66
I2	2.77	2.10
I3	2.85	2.25

The results reveal no particular trend in terms of comparing one sub-catchment with another. It is interesting to note that correlation exists between the clay fraction and the chosen indices of weathering ($r = -0.86^{**}$ and $r = -0.76^{*}$ for SiO_2/R_2O_3 and SiO_2/Al_2O_3 respectively). Such correlations would be expected because of the likely chemical composition of the clay. It is in this context that the ratios may be more a reflection of the clay mineral abundance than an index of weathering.

The analyses of the sediments sampled in the dams of the Mgeni catchment indicate significant correlations between trace element concentration and Al_2O_3, Fe_2O_3, clay mineralogy, and organic matter. These correlations to some extent explain high metal concentrations in certain of the dams. It is believed that many of the associations may be the result of the mineralogical nature of the clays which are a result of the degree of weathering of the catchment soils.

2.5 Conclusion

The Mgeni Catchment is likely to be affected by anthropogenic sources of pollution, particularly from the Pietermaritzburg metropolitan area and other industrial centres. Point source pollution

may often be undetected in routine water sampling and analysis programmes. However, due to accumulatory processes in fine grained sediments of downstream impoundments it may be possible to detect pollution long after the event has occurred.

The nature of the sediment in the impoundments is such that there is a high potential for the accumulation of pollutants as co-precipitated species with minerals present in the clay fraction. This is reflected in significant correlations between the clay content and metals in the sediment. The minerals which are most likely to form sorption complexes with metals are kaolinite, gibbsite and goethite. The minerals have variable charge surfaces and in high pH environments are likely to form electrostatic complexes with cations effectively removing them from solution.

Associations were also observed between Al_2O_3 and Fe_2O_3 with metals. It is envisaged that Al and Fe could occur in the sediments, not only as precipitated minerals, but also as amorphous species. The amorphous Al and Fe oxides have a larger surface area than their crystalline counterparts, and therefore have a higher sorption capacity.

The minerals in the sediments are the result of intense chemical weathering of the soils in the catchment area. The anthropogenic nature of the catchment is, therefore, countered by its natural characteristics.

High concentrations of Mo, Pb and Zn may be explained by the associations between the metals and the clay, Al_2O_3 and Fe_2O_3 concentrations. But such associations do not explain high concentrations of Mn and Cr present in samples I3 and M3 respectively. In the case of sample I3 it was suggested that the Mn concentrations are the result of the accumulation capacity of a particularly fine grained clay fraction. However, this hypothesis would need to be verified by further analytical work. The high concentration of Cr, however, may possibly be due to anthropogenic pollution. Regression analysis suggested that the minerals zircon, ilmenite and quartz occur predominantly in the sand fraction of the sediment.

The characteristics of the impoundment sediments, and in particular the clay mineralogy, are the result of intense chemical leaching of soils in the catchment area, and sedimentary processes. The combination of these two processes has resulted in the formation of sediment material which may

effectively bind metals as sorbed species. Such characteristics imply that the sediments in the Mgeni Impoundments may be ideal for detecting pollution events.

CHAPTER 3

THE PHOSPHATE SORPTION AND DESORPTION CHARACTERISTICS OF MGENI SEDIMENTS

3.1 Introduction

Phosphorus dynamics in aquatic systems are complex processes, resulting from the interaction of P with specific characteristics of the aquatic system - including physical, chemical and biological characteristics. In the Mgeni Impoundments the dominant process which is likely to influence P distribution is chemical and involves the reaction between suspended particles and P. Chemisorption or precipitation reactions may be involved and these are grouped together under the term sorption.

Van der Molen (1991) suggests that P sorption is probably the most effective way in which P can be removed from solution, rendering it no longer readily bio-available under similar environmental conditions. Suspended material is, therefore, an effective P sink. P release from sedimented material is a function of aquatic environmental change which may be sufficient to result in the sediments being a source of readily bio-available P.

A study of P dynamics in aquatic systems, therefore, requires an understanding of sediment-P interactions (Pailles & Moody, 1992) and the environmental conditions which affect them. The characterisation of sediment-P interactions is generally derived by experimentation. Such experimentation often results in the construction of P sorption isotherms. Sediments with different P sorption characteristics may be differentiated from one another by indices derived from these isotherms. In conjunction with analyses of the kind presented in the previous chapter, such information can assist the interpretation of P sorption differences between sediments of different origin.

Experimentation may also be used to interpret the influence which aquatic environmental changes are likely to have on the P sorption characteristics of the sediments. In aquatic systems, the

environmental changes which could be expected to result in changes in sediment P sorption characteristics are those producing changes in pH and redox conditions (Furumai & Ohgaki, 1982). Such changes may influence both the sediment and the overlying water body and, especially, the distribution of P between the two phases.

Although most P sorption takes place onto suspended material, it was thought that a study of the benthic material would be of greater significance, especially since the benthos consists of accumulations of suspended material (Ballinger & McKee, 1971). Furthermore, P release from sediments is most likely to take place from the benthos.

Bainbridge *et al.* (1994) found that soils from Natal generally have a high sorption capacity for P. They note that the highly weathered soils which are dominated by the presence of 1:1-type clays, have especially high sorption capacities. Such soils are extensive in the catchment area and it is, therefore, anticipated that similar, high sorption capacities would characterise the sediments from the Mgeni impoundments.

The objectives of this study are to confirm whether the high P sorption capacity of the catchment area soils is recognisable in the impoundments and to determine the extent to which environmental changes are likely to influence the P sorption capacity of the sediments.

3.2 Phosphorus sorption isotherms

Phosphorus sorption isotherms describe the experimental relationship between the amount of P sorbed and the P concentration in solution at equilibrium. The reaction between P and sediment is highly sensitive to experimental conditions. Barrow (1978) recognised a number of factors which could influence sediment P sorption under experimental conditions. These include: the period and temperature of contact between soil and solution; the method of shaking; the sediment:solution ratio; the nature and concentration of supporting electrolyte; the moisture content of the soil prior to shaking; and the concentration of P in the sediment. Controlling these factors is necessary for consistency in the results.

Sposito (1989) suggests for soils that there are four categories of sorption isotherms: the S-, L-, H-, and C-curves. The L-curve is the one most commonly found in soil conditions and is distinguished by a steep initial slope which is seen to ease with further increases in the concentration of P in the equilibrium solution. The L-curve results from a high proclivity of the sediment particles for P at low P concentrations. As P concentrations increase there is a decreasing number of sorbing surfaces resulting in an excess of P in solution. Essentially, the L-curve indicates that the energy of sorption decreases exponentially with increasing saturation of the sorbing surface (Bache & Williams, 1971).

Barrow (1984) suggests that there are essentially two reasons for employing sorption isotherms. The first is to attempt to learn more about the nature of the sorption process. The second is to provide numerical indices which allow the sorption properties of the sediment to be described quantitatively without having to refer directly to curves. The derived indices can then be related to one or more properties of the sediment, which may help to indicate which sediment attributes are most likely to contribute to the P sorption reaction.

Several mathematical equations have been devised for describing sorption isotherms. Those which are most commonly used are the Langmuir, van Bemmelen-Freundlich, and Temkin equations. P sorption isotherms may also be described on the basis of single point indices, examples of which include: the P sorption at a chosen P equilibrium concentration and the P sorption from a constant concentration of P added (Bache & Williams, 1971).

Each of the described methods has been noted as having some inherent flaws. For a detailed discussion of potential errors in using these techniques, the reader is directed to Bache & Williams (1971) and Barrow (1978).

3.3 Experimental techniques

It is essential to the construction of sorption isotherms that the conditions are kept stable throughout the experiment. Temperature stability was attained by equilibration in a laboratory environment in which temperature fluctuations were kept to a minimum. The shaking speed for all of the proceeding experiments was kept constant. All of the sorption and desorption work was

carried out by batch experimentation, where the reaction was forced by shaking a fixed mass of sediment with a fixed volume of P solution.

3.3.1 P sorption

A 2.5 g, ground and dried, sample of sediment was weighed into a 50 ml centrifuge tube to which 25 ml of P solution was added. The P solutions were made up in a 0.1 M NaCl matrix. The initial P concentrations were 0, 0.25, 0.5, 1, 2.5, 5, 10, 20, 40, 80 and 100 mg/l. The centrifuge tubes were capped with cork bungs covered with parafilm to prevent contamination, and shaken horizontally on a reciprocal shaker for 24 hours. Barrow (1978) suggests that P sorption reactions are mostly complete in 24 hours but that limited sorption may continue indefinitely. He found that sorption reactions continued after 1000 days in similar experiments. After 24 hours the tubes were centrifuged at 6000 rpm for 5 minutes. The supernatant was decanted through Whatman no. 1 paper and stored for P determination by the Murphy & Riley (1962) technique (Appendix B). The pH of the supernatant was also measured. The residue was retained in the centrifuge tubes for later desorption studies.

3.3.2 P desorption

A 0.1M NaCl P-free solution was added to the sediment residue from the P sorption experiments. The suspensions were thoroughly mixed and equilibrated for 24 hours. The supernatants were separated and anlysed for P and pH as described for P sorption above.

3.3.3 Effect of pH on sorption

The effects of pH on P sorption by the three Inanda samples was studied by the construction of sorption envelopes which are plots of the amount of P sorbed as a function of equilibrium pH (Sposito, 1989). In order to construct sorption envelopes it was necessary to adjust the initial pH of the added solutions, by means of acid or base additions.

The sediment:solution ratio was the same for the initial P sorption study, although a different range of P concentration solutions was used. The initial P concentrations chosen were 0, 2.5, 5, 10, 20,

40, 60, 80 and 100 ppm. The suspensions were shaken until a slurry had formed. The pH of the slurry was determined and then adjusted by drop-wise addition of either 0.1M HCl or 0.1M NaOH. Five different initial pH regimes were chosen. The centrifuge tubes were then shaken on a reciprocal shaker for 1 hour, after which time the slurry was centrifuged and the supernatant filtered and retained for analysis as described in Section 3.3.1.

3.3.4 Effect of redox on sorption

3.3.4.1 Sample preparation

In order to determine the effect of redox conditions on the sorption of the Inanda samples it was decided to reduce the samples prior to experimentation. The reduction was achieved by promoting microbial activity in the sediment by thoroughly mixing approximately 150 g of sediment with 50 ml of a glucose ($C_6H_{12}O_6$) solution. The containers were sealed to prevent air from causing further oxidation. The samples were stored at a constant temperature for 7 days. A sub-sample of the slurry was then removed to determine the solids concentration prior to experimentation.

3.3.4.2 Experimentation

A quantity of the reduced homogenised slurry containing 2.5 g of sediment (on an oven-dry basis) was weighed into 50 ml centrifuge tubes. Twenty ml of a 40 mg/l P solution, made up in a 0.1M NaCl matrix, was added to the sediment. Five ml of a particular concentration of reducing or oxidising agent was added to the slurry after which the tube was immediately sealed to prevent any changes in redox status. To achieve a range of reducing conditions $Na_2S_2O_4$ was added at concentrations of 0.0625, 0.125, 0.250, and 0.5 M. Oxidation was achieved by the addition of H_2O_2 at concentrations of 0.125, 0.25, 0.5, and 1 M. The suspensions were equilibrated on a reciprocal shaker for 24 hours. After that time the redox potentials and the pH of the slurries were determined (Appendix B). The slurries were centrifuged and the supernatants analysed as described previously (Section 3.3.1).

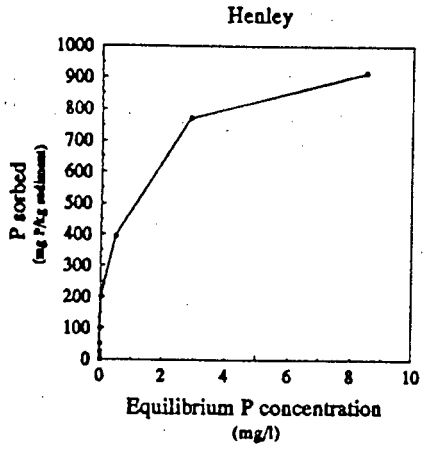
3.4 Results

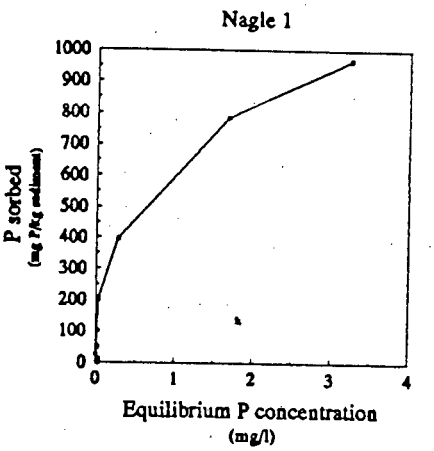
The raw data from the experimental work is detailed in Appendix C, along with any data manipulation and supplementary figures required for the proceeding discussion.

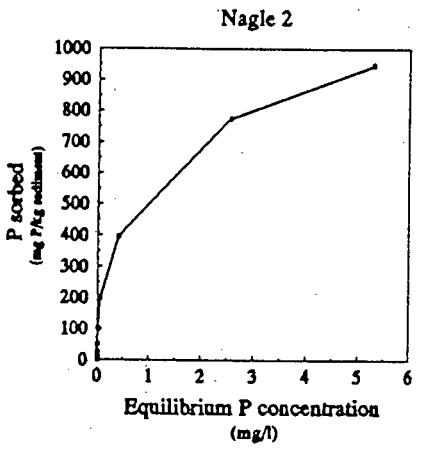
3.4.1 P sorption

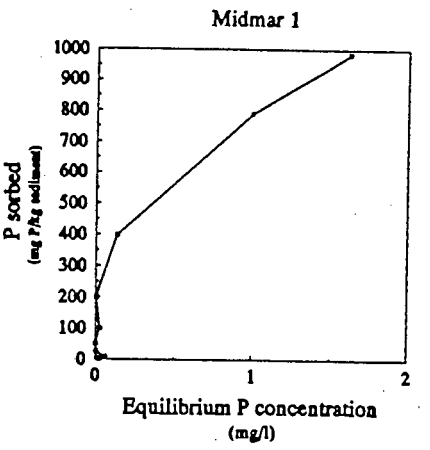
Appendix C (Part 1) details the results of the P sorption experimentation carried out without pH adjustment. On the basis of these results, the amount of P sorbed was plotted against the equilibrium P concentration (Figure 3.1). The isotherms can broadly be described as conforming to the L-shape isotherms described by Sposito (1989), suggesting that there is a high affinity of the sediment for P at low concentrations which diminishes exponentially as the surfaces become increasingly saturated with P.

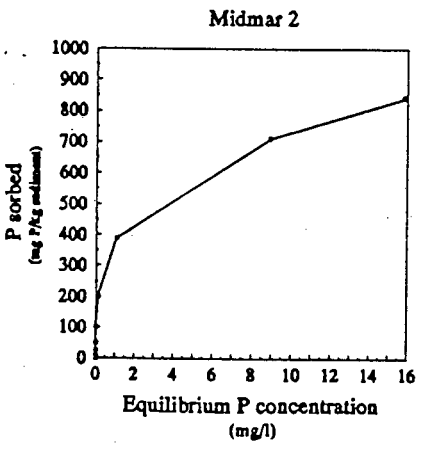
To differentiate quantitatively between the P sorption characteristics of the sediments, sorption indices were derived. It was decided that the Langmuir and Freundlich equations were not suitable for describing the isotherms. The sorption index derived from a Langmuir-type equation, the sorption maxima, is more a function of the amount of P initially added (experimentally) than particular sediment properties. The Freundlich equation has limited application. The Freundlich equation is dependent on the assumption that a straight line could be fitted to the data and it is seldom possible to fit such a line. These limitations suggested that another approach be used. A highly pragmatic approach was chosen.











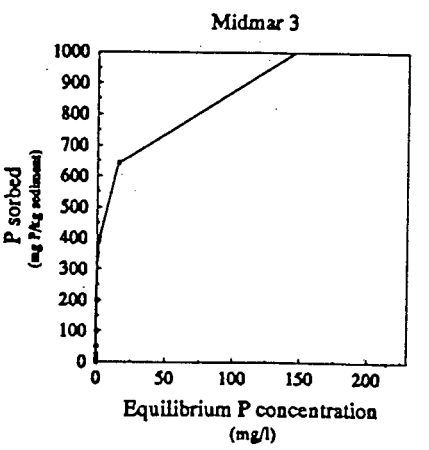


Figure 3.1 Phosphorus sorption isotherms for the Mgeni Catchment sediments

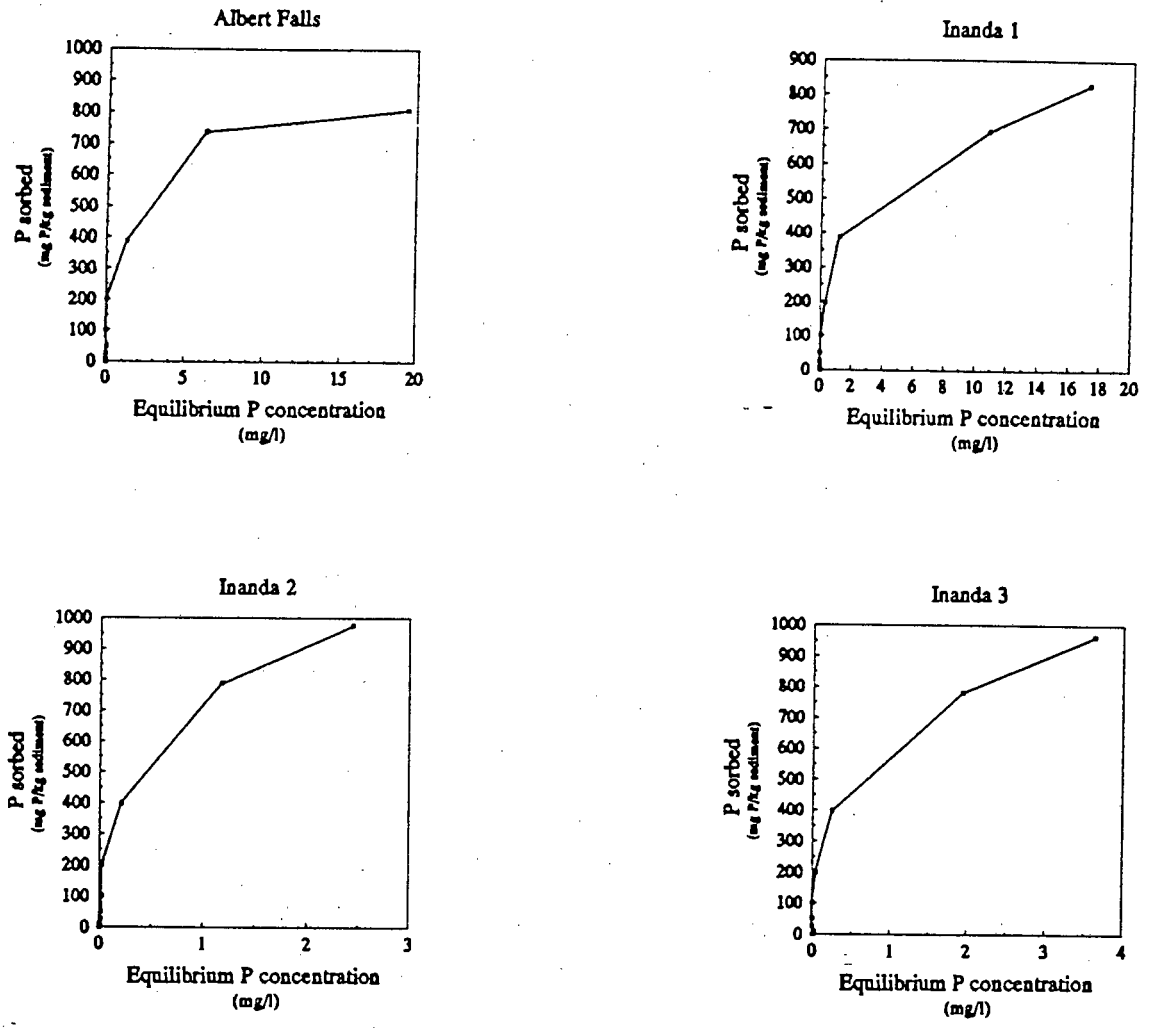


Figure 3.1 (cont.) Phosphorus sorption isotherms for the Mgeni Catchment sediments

The sorption isotherms were described by the amount of P sorbed at a chosen P equilibrium concentration. Bache & Williams (1971) indicate that such an approach also has limitations. Bache & Williams (1971) indicate that a single point describes the isotherm at one particular concentration and does not allow for further interpretation at other concentrations. To overcome this potential problem it was decided that two equilibrium concentrations would better describe the isotherm. The sorption indices derived from Fig. 3.1 are shown in Table 3.1.

Table 3.1 P sorption indices based on 1 and 2 mg/l equilibrium P concentrations

Sample	P sorbed at equil. conc. (mg P/kg sediment)	
	1 mg/l	2 mg/l
H	480	585
N1	575	831
N2	565	725
M1	820	>1000
M2	368	445
M3	50	50
AF	355	520
I1	363	478
I2	780	900
I3	650	800

The 1 mg/l P equilibrium concentration index was chosen because it corresponds with the South African special standard for P effluent into sensitive aquatic systems. The 2 mg/l P equilibrium concentration was chosen for expedient reasons in that it falls within the P equilibrium range of all the isotherms, with the exception of M1 (Fig. 3.1).

The close correlation between the two indices ($r = 0.99$, $p = 0.0001$) confirms that the two indices are derived from the same isotherm and that either could be used as a basis for differentiating

between the sediments. The index derived from the 1 mg/l equilibrium concentration was chosen for this purpose.

P sorption indices (Table 3.1) allow very broad sediment groupings to be recognised. Notably, that samples M1, I2, I3, N1, and N2 have significantly higher sorption capacities than the other samples.

3.4.2 Sediment characteristics influencing P sorption

In order to interpret the geochemical significance of the P sorption index, and to explain differences observed between samples, it is necessary to explore the relationships which may exist between P sorption and particular sediment characteristics. To achieve this objective, regression analysis was carried out between the P sorption index and various sediment properties. The results are shown in Table 3.2.

Table 3.2 Correlation coefficients between the P sorption index (1 mg/l) and and selected properties of the sediments

Content (%)	Correlation coefficient
SiO_2	$-.76^{**}$
Al_2O_3	$.80^{**}$
Fe_2O_3	$.72^{*}$
MnO	.30
MgO	$.77^{**}$
CaO	.04
Clay	$.74^{*}$
Sand	$-.76^{*}$
LOI	.58
pH	-.23
SiO_2/Al_2O_3	$-.82^{**}$
SiO_2/R_2O_3	$-.82^{**}$
R_2O_3	$.82^{**}$

(n=10, ** = $p<0.01$, * = $p<0.05$)

The results indicate a highly significant positive correlation between the P sorption index and Al_2O_3, MgO, and R_2O_3 contents, and a highly significant negative correlation with SiO_2, SiO_2/Al_2O_3, and SiO_2/R_2O_3. Less significant correlations are also shown, positively between the P sorption index and Fe_2O_3 and clay, and negatively with sand. The significance of each is discussed below

3.4.2.1 Influence of clay content

The fine grain size of the clay content readily explains the correlation between this material and the P sorption indices. Wild (1988) suggests that the greater the surface area of a material the higher is its potential to sorb and that surface area influences are potentially more important than the composition of the clay fraction. If this were the case then sample I3, having the largest clay content, would be expected to have a higher sorbing capacity than the other samples. As this is not the case it is conceivable that the clay type also plays an important role.

Tisdale *et al.* (1985) state that 1:1 layer silicate clays (e.g. kaolinite) are likely to sorb more P than 2:1 layer clays. The presence of high concentrations of Al and Fe oxides, is often indicative of kaolinitic materials (Tisdale *et al.*, 1985). In low pH regimes a positive surface charge is expected with kaolinitic material, promoting electrostatic attraction with the P ligand.

Kaolinite is abundant in all of the sediments and, without quantitative XRD data, cannot be used to differentiate between them. The presence of kaolinite indicates an advanced stage of weathering, especially when it is accompanied by accessory amounts of goethite and gibbsite, as was identified in most of the sediment samples (Sposito, 1989). It is, therefore, envisaged that the ratio SiO_2/R_2O_3 may broadly indicate the concentration of kaolinite in the samples. The data presented in the previous chapter show that the SiO_2/R_2O_3 ratios for the samples are essentially similar, with the possible exception of samples I2 and I3.

The significant negative correlation between the P sorption indices and SiO_2/R_2O_3 suggests that the higher the degree of weathering, indicated by a low ratio value, the higher is the sorption capacity of the sample.

3.4.2.2 Influence of Al and Fe oxides

Froelich (1992) disputes the influence that "pure" clay minerals, e.g. kaolinite, have on P sorption. He suggests that the sorbing influence of clay minerals is noteworthy during the initial rapid stage of sorption but has no significance during the later slow sorption stages, and that the presence of Al and Fe oxide species has a greater influence on P sorption, noting that it would be virtually impossible to determine the sorption capacity of clay minerals without taking Al and Fe oxides into account.

The correlation between Al_2O_3 and Fe_2O_3 contents with the P sorption indices is highly significant. Crystalline minerals, such as gibbsite, hematite and goethite, as well amorphous coatings on clay surfaces will contribute to the Al_2O_3 and Fe_2O_3 contents, as will silicate clay minerals. The relative influence which each of the species has on P sorption is highly variable. It is important to mention that the XRFS analysis for Al_2O_3 and Fe_2O_3 makes no differentiation for the form or species distribution of the elements in the sediments. However, one can assume some species relationships.

It is conceivable that the P sorption capacities of the sediments are mostly influenced by the Al_2O_3 and Fe_2O_3 concentrations. In sediments where the influence of these elements is so prevalent it is their crystallinity which has the greatest control on sorption. It has been shown that the less crystalline a species, the higher is its P sorption capacity (Tisdale *et al.*, 1985; Singh & Gilkes, 1991). Although amorphous Al_2O_3 and Fe_2O_3 have a greater P sorption capacity than their crystalline equivalents, the crystalline forms have a greater sorption capacity than do "pure" clay minerals.

Lucotte & d'Anglejan (1988) note that P sorption by Al_2O_3 and Fe_2O_3 can take place through two processes, the results of which are essentially similar. The first process, co-precipitation, results when P reacts with Al_2O_3, or Fe_2O_3 resulting in newly formed solid precipitates. The second process of adsorption is probably more common in the sediments and is often the result of ligand exchange between P and OH^- ions on hydrous Al_2O_3 and Fe_2O_3 surfaces. This will often take place on clay minerals which are coated with Al and Fe oxides or may take place onto distinct Al or Fe hydroxide mineral surfaces. The process of ligand exchange is dependant on the activity of OH^- in

solution and is, therefore, closely related to pH. Both of the processes dominate in the secondary "slow" stage of sorption.

It is fairly evident from the correlations presented (Table 4.2) and the preceding discussion that the P sorption characteristics of the sediment are dominated by reactions of P, either with Al or Fe oxides, or with kaolinite. Considering these factors it is likely that changes in pH and redox conditions would result in alteration of sediment P sorption characteristics.

3.4.3 Effect of pH on P sorption

It is generally accepted that an increase in pH will reduce the P sorption capacity of sediments, particularly in sediments where Ca is not influential in the sorption process. Such a trend is evident in Figure 3.2 which shows a noticeable decrease in the P sorption capacity with an increase in pH.

Fig. 3.2 is a plot of sorption indices derived from sorption isotherms which appear in Appendix C (Part 2) against the equilibrium pH of the sediment slurry. The indices are based on a 20 mg/l P equilibrium concentration.

A few trends are evident from the plot. The most obvious inference which could be drawn from Fig. 3.2 is that the sorption indices of the sediments noticeably decrease as the pH increases and that the most significant decrease takes place between about pH 5.2 and pH 7.

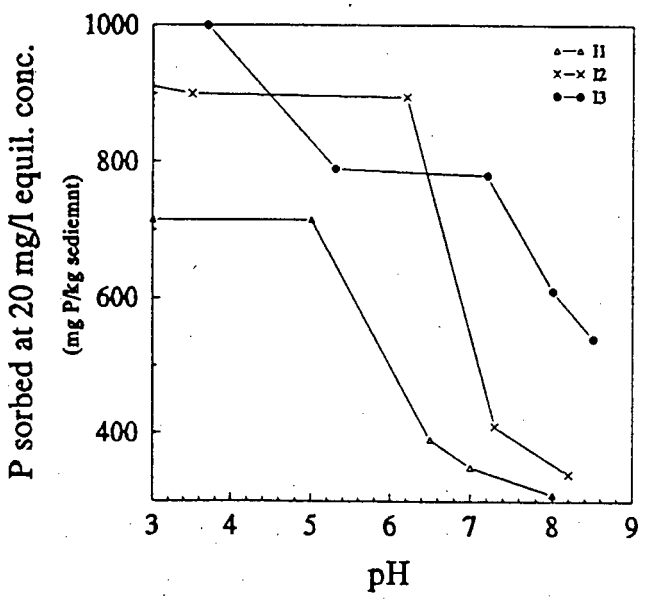


Figure 3.2 Sorption envelope for the Inanda dam samples

The major reason for a decrease in the P sorption capacity of the sediments with an increase in pH is related to the surface charge on the sorbing plane. Aluminium and iron oxides, and kaolinite are amphoteric (Tisdale *et al.*, 1985). The charge on the surfaces of these species is largely dependent on the pH of the solution with which the sediments are in equilibrium. Low pH conditions promote positive surface charges which will result in strong electrostatic attraction between the surface and P. As pH increases, however, the activity of OH^- increases resulting in enhanced competition between itself and P for sorption sites. A negative surface charge may also result.

The point of zero charge, a pH condition where there is no surface charge, is at approximately pH 8.5, 9, and 7 for Al_2O_3, Fe_2O_3 and kaolinite respectively (Tisdale *et al.*, 1985). Tisdale *et al.* (1985) further state that gibbsite sorbs a maximum amount of P around pH 4-5 while the sorption capacity of goethite decreases consistently between pH 3-12.

The fairly close agreement between the pH conditions at which the sorption indices are seen to decrease and the pH conditions at which decreases would be expected for gibbsite, goethite and kaolinite, seems to confirm that these minerals are most likely to control P sorption. The limitations of this statement will become evident after the later discussion of mineral solubility.

3.4.4 Effect of variable equilibrium redox conditions on P sorption

The P sorption experiments which were carried out over a range of redox conditions broadly indicate that there is a significant decrease in the sorption capacity of sediments with a decrease in the redox conditions. This trend is evident in Figure 3.3.

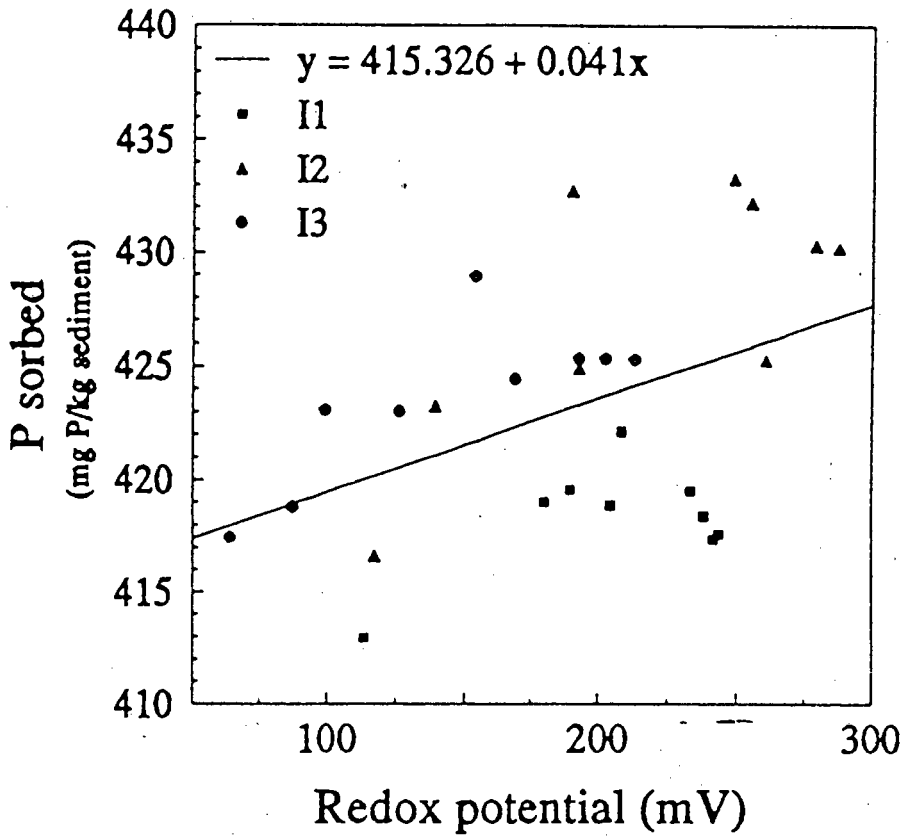


Figure 3.3 P sorption plotted against the equilibrium redox potential for the Inanda samples

(r = 0.45, p = 0.02, n = 27)

The differences in the P sorption capacities of the variably reduced sediments are not pronounced, a factor reflected in the shallow gradient of the regression equation. Regression lines were attempted for individual samples but no significant correlations between P sorbed and redox potential were found for any of the samples. The results depicted in Fig. 3.3 are not directly applicable to field conditions as no *in situ* redox measurements were taken in the impoundments.

It is interesting to note that, although, under a range of redox conditions, sample I1 still has a lesser sorption capacity than samples I2 and I3, it can, however, be empirically observed that the differences are less under reducing conditions than under more oxidising conditions. Furthermore the differences between the P sorption capacity of the most reduced samples and oxidised samples are more marked for samples I2 and I3 than for sample I1. It is envisaged that the higher concentrations of Fe_2O_3 in sample I2 and I3 are responsible for these observations.

Furumai & Ohgaki (1982) state that the sediment Fe content is most likely to be influenced by reducing conditions. The reduction of Fe^{3+} to the more soluble Fe^{2+} may be responsible for a decrease in sorption capacity under reducing conditions. The presence of Al oxides and kaolinite, as sorbing species is likely to buffer this effect. Such buffering is probably responsible for the similarity in sediment P sorption characteristics, within individual samples, at all but the most pronounced reducing conditions.

3.4.5 P desorption

Significant changes in pH and redox conditions are required to induce P desorption from sediments. Therefore, under oxidised and neutral pH conditions desorption is likely to be limited. This trend is fairly evident in the desorption results presented in Appendix C (Part 4) which reflect low P equilibrium concentrations. Figure 3.4 is an unconventional representation of the data, but one which clearly shows that most of the P added to the sediment was sorbed and was not readily desorbed on washing the sediment with a P-free solution.

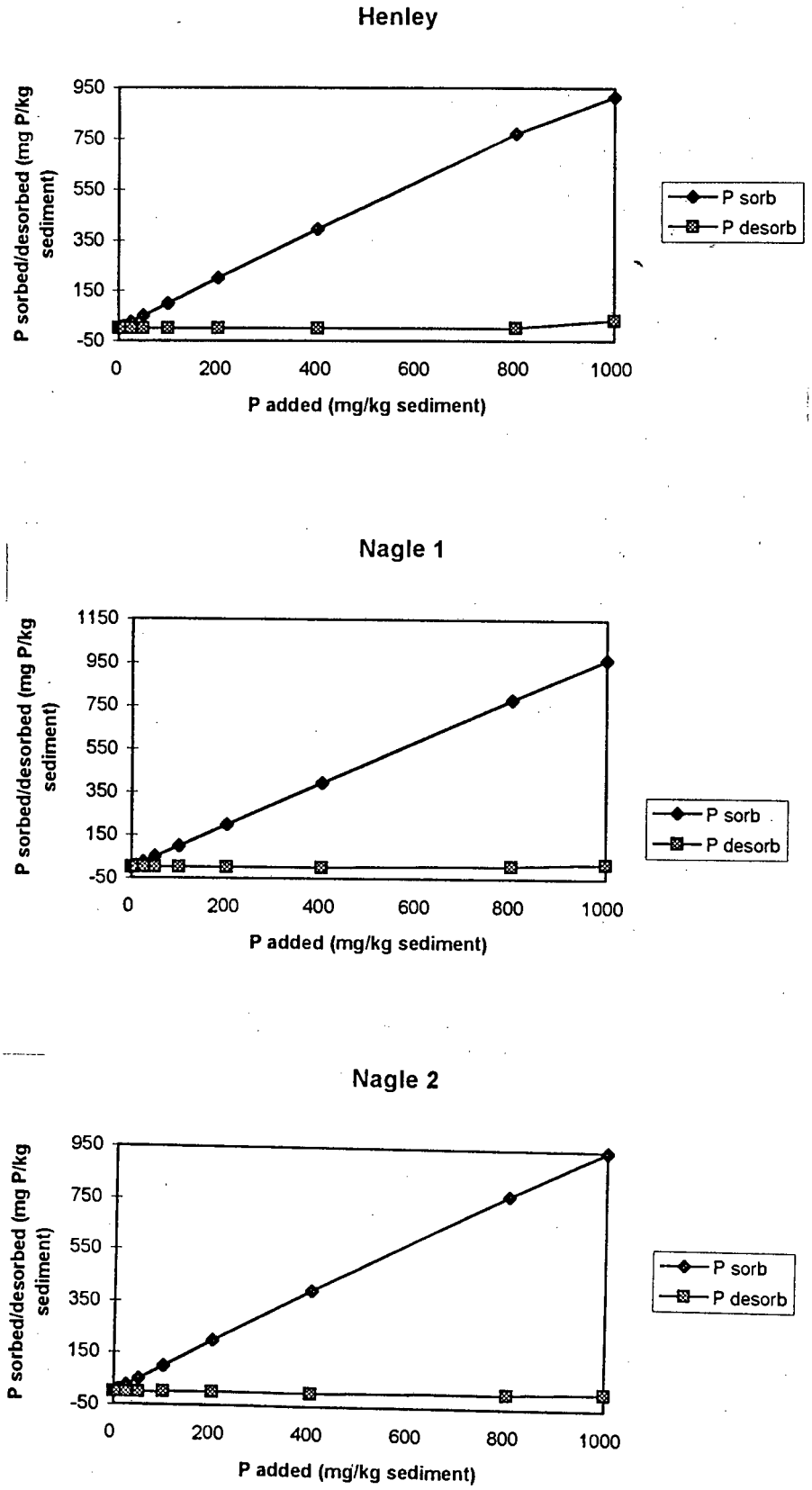
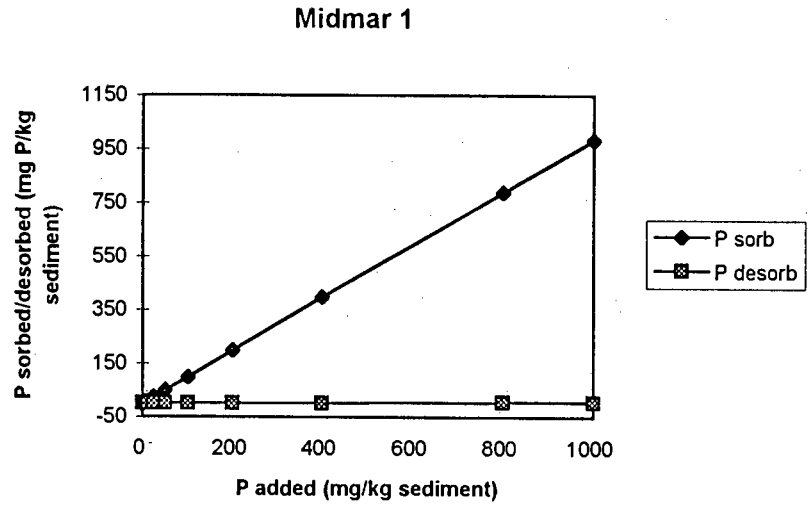
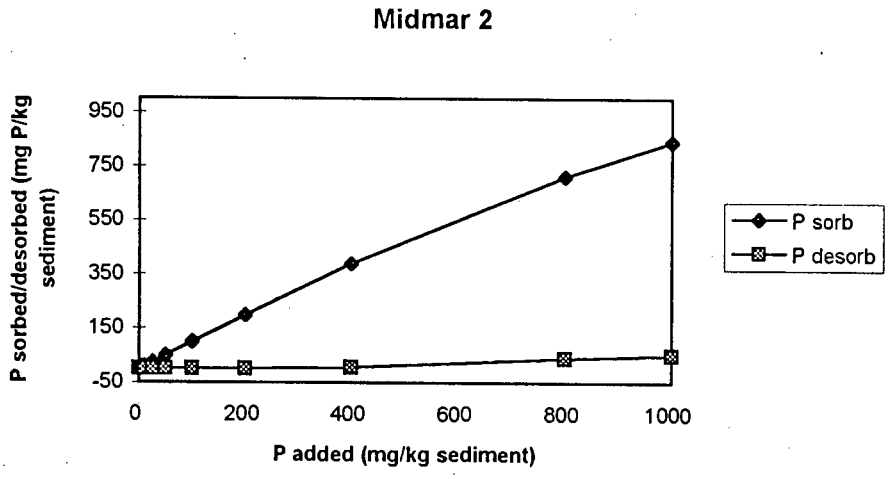


Figure 3.4 P sorption/desorption plotted against amount of P initially added





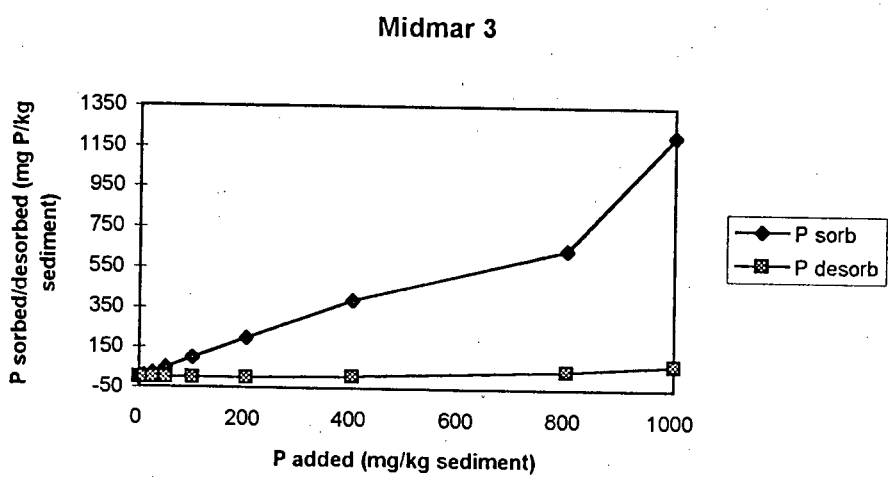


Figure 3.4 (cont.) P sorption/desorption plotted against amount of P initially added

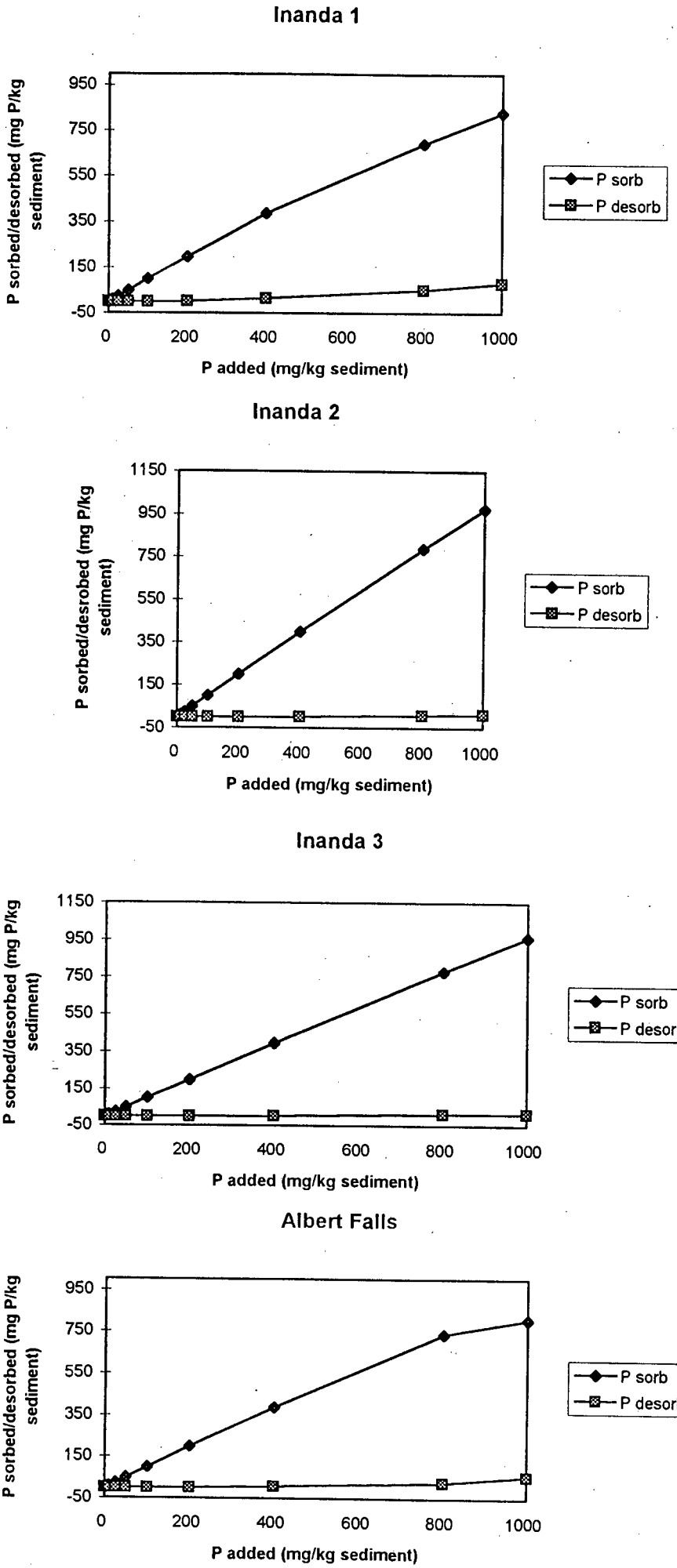


Figure 3.4 (cont.) P sorption/desorption plotted against amount of P initially added

3.4.6 A basis for predicting the P sorption index of Mgeni sediments

It is evident from the preceding discussions that the P sorption characteristics of the sediments from the Mgeni Catchment are mostly influenced by the presence and concentration of Al_2O_3 and Fe_2O_3 and by the abundance and mineralogy of the clay-size fraction. It is possible that these parameters could be used as predictors of the P sorption index for sediments taken from the Catchment. The laborious nature of experimentally determining a sorption index for a sediment suggests that a short-cut method be derived for determining the index.

To obtain the most predictive equations for determining the P sorption indices, stepwise regression analysis was attempted It was found that no two variables used conjunctively could improve the predictive equations that derived from the correlations of P sorption index and SiO_2/R_2O_3 and R_2O_3. Figure 3.5 depicts the correlation plots between these two variables and P sorption index. As there is no difference in the correlation coefficients of the two plots, either parameter could be used to predict P sorption indices.

It is evident that XRFS analysis of the major elemental concentrations of the sediments will allow one to make broad predictions of the sorption properties of other sediments in the catchment. It should, however, be pointed out that the predictive equations are based on the parameters measured within the confines of this study and that improved equations may be derived from other parameters. Bainbridge *et al.* (1994), for example, found that the P sorption index correlated significantly with oxalate-extractable Al.

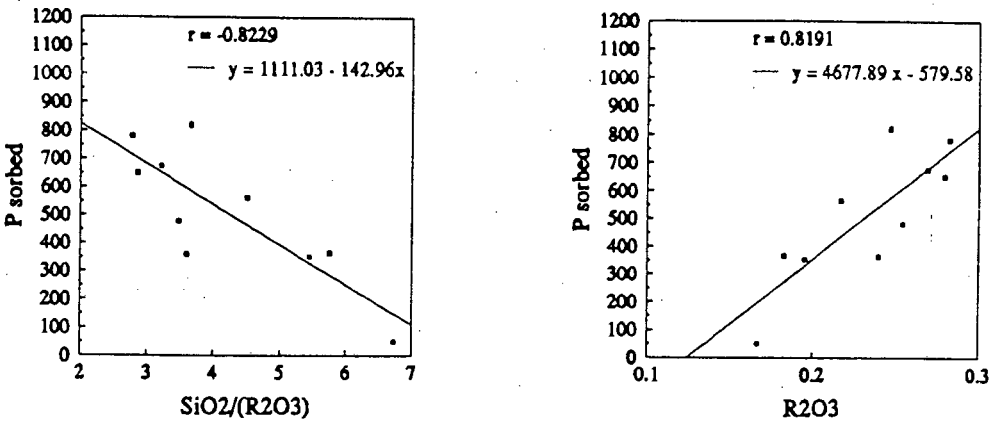


Figure 3.5 Correlation plots for P sorption index and the most likely predictive parameters

It is envisaged that, if the ratio SiO_2/R_2O_3 correlates most significantly with the P sorption characteristics of the sediments, then it is likely that quantitative mineralogical analysis of the clay fraction would possibly render similar results, although such a study would be complex and possibly more laborious than P sorption experimentation.

3.5 Phosphate equilibria and distribution in impoundment water

3.5.1 Introduction

This chapter, so far, has dealt mostly with the reactions of P with sediment particles and has predicted that most, and in some cases all, of the P equilibrated with the sediment would be sorbed. No particular mechanism for sorption has been discussed but it is envisaged that chemisorption is most likely to have occurred, this hypothesis being based on the assumption that no precipitation is

likely to have occurred under the experimental conditions used. The fact that precipitation has not been considered limits the applicability of this study since other ions in an aquatic system interact with P as well. The net result of precipitation is similar to that of sorption in that P is removed from solution. To effectively model and determine the speciation and precipitation reactions of P in the impoundments is was necessary to use MINTEQA2.

MINTEQA2 was designed by the U.S. Environmental Protection Agency (E.P.A.) to predict the equilibrium composition of a water body. The programme utilises quantitative mathematical models to describe the competing processes which affect the overall behaviour of ions in aquatic environments (Allison *et al.*, 1991). MINTEQA2 determines the mass distribution between the dissolved, adsorbed, and precipitated phases under an assortment of conditions. The input data required to run the programme consists of total dissolved concentrations of the relevant components and measures of other environmental parameters which may influence the system, including pE, pH, or the partial pressures of gases. These parameters may be specified as equilibrium values or MINTEQA2 can calculate the values at equilibrium (Allison *et al.*, 1991). MINTEQA2 employs an extensive thermodynamic database which may be supplemented by additional values. No adsorption work was attempted in this study so the limitations of the MINTEQA2 adsorption model will not pose problems for the study.

It was not possible to carry out detailed speciation calculations for water quality data from all of the sampling sites. Sample site I1 was chosen in preference to the other sites as it is situated at the input of Inanda dam and likely to be influenced by inputs of high concentrations of P.

3.5.2 Input data for PRODEFA2

PRODEFA2 is an accessory programme used to input data files for MINTEQA2. The water quality data were supplied courtesy of Umgeni Water. Four samples were selected for speciation calculation. The samples were taken between February, 1990 and October, 1993 from the impoundment surface. Differences in water chemistry between the surface samples and those taken

above the sediment water interface have been assumed to be negligible. Measurements of temperature and pH were taken *in situ*. The water quality variables and concentrations are detailed in Table 3.3.

Table 3.3 Water quality data for a sample taken near to site I1

Water quality variable (mg/l)	Date sampled			
	08/02/90	13/12/90	07/10/91	07/10/93
Calcium	13.3	10.4	14.8	13.8
Magnesium	6.06	5.6	7.37	7.34
Sodium	13.2	20.9	26.9	33.0
Potassium	2.7	2.4	7.27	3.78
Ammonia	0.06	0.02	0.04	0.04
Iron	0.42	0.5	0.40	1.66
Chloride	28.3	26.2	31.3	37.8
Fluoride	0.18	0.15	0.07	0.23
Sulphate	12.2	12.2	13.4	36.1
Phosphate"	287×10^{-3}	5×10^{-3}	15×10^{-3}	8×10^{-3}
Carbonate	31.1	29.1	33.4	36.1
Silica	4.3	6.8*	6.1	2.1
Manganese	0.02	0.04	0.02	0.05
Aluminium	110×10^{-3}	6.5×10^{-3}	65×10^{-3}	65×10^{-3}
pH	8.6	8.3	8.4	7.1
Temperature (°C)	27.3	29.2	20.0	20.6

* no silica value was available for the day when the sample was taken so a typical value for the same site was assumed

" the concentration is for Soluble Reactive Phosphate.

The equilibrium calculations were carried out using the Davies equation. The analyses (Table 3.3) are of the dissolved concentration in water, therefore oversaturated solids were not allowed to precipitate. Iron and manganese were entered as their reduced (Fe^{2+} and Mn^{2+}) species.

3.5.3 Results and discussion

The equilibrium speciation of phosphate is shown in Table 3.4.

Table 3.4 Equilibrium distribution of phosphate species in solution

Species	% Composition
$MgPO_4^-$	4.3
$MgHPO_4$	8.1
$CaPO_4^-$	6.7
$CaHPO_4$	3.6
$FeHPO_4$	1.6
$H_2PO_4^-$	4.7
HPO_4^{2-}	70.7

The result that $H_2PO_4^-$ and HPO_4^- are the dominant dissolved species was expected because they are reported to be the predominant dissolved P species over the pH range 5 to 9 (Stumm & Morgan, 1970). The data reveals the formation of a number of metal P complexes. Changes in environmental conditions (pH and pE) may change the distribution of P in solution and may result in the precipitation and formation of other P complexes.

To model these interactions the chemical equilibrium data sample was used to construct a unified solubility diagram for various Ca, Al, and Fe phosphates (Figure 3.6). The solubility diagram was constructed for the most commonly occurring phosphate minerals in aquatic systems. The minerals, and their chemical composition are shown in Table 3.5.

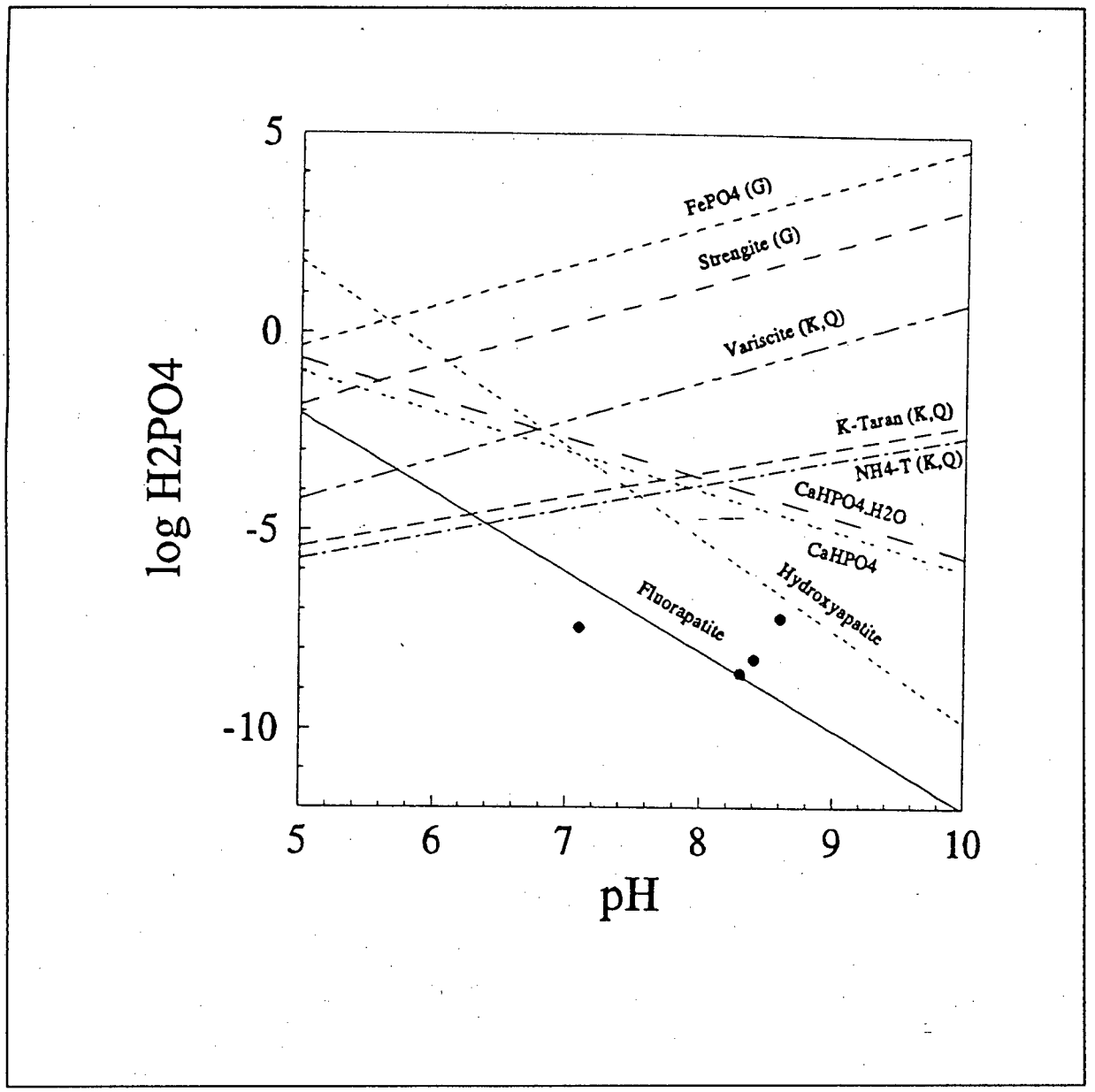


Figure 3.6 Unified solubility diagram of the predominant Ca, Al and Fe phosphates in aqueous systems (where $Ca^{2+} = 2.5 \times 10^{-4}$ M, $K^{+} = 6.1 \times 10^{-5}$ M, $F^{-} = 7.8 \times 10^{-6}$ M, $NH_4^{+} = 9.7 \times 10^{-7}$ M)

(where • indicates samples input into PRODEFA2 as reflected in Table 3.3;and: G = goethite; K = kaolinite; Q = quartz; K-Taran = taranakite; NH_4 -T = NH_4-taranakite

Table 3.5 Common P minerals in aquatic systems (after Lindsay, 1979)

Mineral	Chemical composition	log K°
Variscite	$AlPO_4.2H_2O$	-2.50
K-taranakite	$H_6K_3Al_5(PO_4)_8.18H_2O$	-22.30
NH_4-taranakite	$H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$	-19.10
$FePO_4$ (c)	$FePO_4$	-5.37
Strengite	$FePO_4.2H_2O$	-6.85
Brushite	$CaHPO_4.2H_2O$	0.63
Monctite	$CaHPO_4$	0.30
Hydroxyapatite	$Ca_5(PO_4)_3OH$	14.46
Fluorapatite	$Ca_5(PO_4)_3F$	-0.21

The solubility lines of the Al minerals were constructed under the assumption that the water was in equilibrium with kaolinite and quartz. This assumption was chosen because it is plausible that the analysis for Al^{3+} may have included colloidal material. A similar assumption was made for Fe which was likely to be in equilibrium with goethite.

Figure 3.6 indicates that the solubility of P in the system is controlled by the activity of Ca-phosphate minerals, most noticeably hydroxyapatite and fluorapatite. It is likely that the apatite-like minerals will remain the most stable P minerals down to a pH of approximately 6.4, unless there is a significant change in the activities of Ca^{2+}, F^-, NH_4^+, or K^+, resulting in a shift of the related solubility lines. The other alternative to alter solubility would be to significantly increase the activity of P. Water quality data from Inanda dam reveals that the significant chemical changes required to alter P solubility have not been experienced.

The stability of the precipitated minerals is unlikely to be greatly influenced by a decrease in redox potential. Lindsay *et al.* (1989) note that Fe and Mn phosphate minerals are most likely to be influenced by reducing conditions, therefore, excluding the Ca minerals which are likely to be in equilibrium with the aqueous system.

3.6 Conclusion

The P sorption characteristics of the Mgeni Catchment sediments are the result of the chemical and physical properties of the sediments. Clay content is the physical property which is most likely to influence the P sorption capacity of the sediment. Although particle size distribution of the samples had a large influence on the P sorption capacity, it is the chemical and mineralogical nature of the clay fraction which is likely to have a greater influence.

The presence of kaolinite, gibbsite, and goethite in the clay fraction is indicative of a highly weathered material and results in high P sorption capacities for the sediments. The strong correlation between the index of weathering and the P sorption index suggests that the P sorption characteristics of the sediments may be correlated with the intensity of weathering of the soils from the catchment.

The suggestion that P sorption is most likely to be influenced by reactions with Al_2O_3, Fe_2O_3 and kaolinite is supported by experimental evidence showing that with increased pH there is a noticeable decrease in the sorption capacity of the sediments. Such a response would be expected if sorption were onto surfaces of variable charge. Surface charge in these cases is influenced by the presence of hydroxyl or hydrogen ions on the surfaces - the distribution of these ions being dependent on pH. The influence of redox on P sorption capacity is mostly confined to a control on the solubility of Fe_2O_3 in the sediments. Changes to more reducing conditions possibly result in the reduction of ferric to ferrous iron. Ferric iron oxides are the species onto which P is preferentially sorbed.

MINTEQA2 speciation data indicates that the activity of P and the pH of the solution plots in the hydroxyapatite/fluorapatite window, suggesting that these are the minerals which are likely to control the solubility of P and would remain so within field pH conditions, down to about pH 6.4, where the Fe and Al phosphate precipitates are likely to be more stable.

It is not possible to conclude whether precipitation or sorption is going to account for the P in solution at equilibrium (Stumm & Morgan, 1970). Fey (1988) concludes that neither process should be invoked without reference to, or consideration of, the other. Speculation about which

process is likely to be the most relevant in the removal of P from solution in the Mgeni system is not plausible and will not be attempted.

4. CONCLUSION

A geochemical study of sediments taken from five impoundments in the Mgeni catchment, Henley, Nagle, Midmar, Albert Falls and Inanda dams, was undertaken to try and understand how the sediment will interact with phosphorus pollution.

The results of this study have indicated that the sediments in the impoundments are likely to remove, from solution, most if not all of the P being input into the impoundments, especially in acidic, oxidising conditions. The P that is sorbed is not readily released indicating that it is effectively "locked up". These P reactions compete with complexation reactions of P with other ions in solution which result in the possible precipitation of Ca-phosphate minerals.

It is not possible to speculate as to which of the processes is most likely to be dominant, and it is suggested that such a speculation may not be overly necessary because the net result of both of the processes is the removal of P from solution, thereby limiting the potential of P pollution in the system.

These conclusions do not suggest that P should blithely be ignored as a potential pollutant, but the results do imply that the receiving capacity of the sediments is such that the problems of eutrophication may not be as significant as initially believed.

The study of sediment P sorption characteristics is certainly a hackneyed one, as is evident by the large body of literature available on the subject. This thesis is in no way an attempt to add to the global understanding of the subject but is rather an application of previous studies to a particular system, in an attempt to better understand that system, thereby enhancing the body of knowledge about the Mgeni Catchment and providing a strong scientific basis for the environmental management, with respect to P, of the catchment and its impoundments.

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APPENDIX A - AREAL PROPORTION OF MGENI CATCHMENTS OCCUPIED BY DIFFERENT LITHOLOGIES AND LAND USE

A.1 Areal proportion of Mgeni impounddment catchments occupied by different lithologies (Source: Umgeni Water)

Impoundment	Lithology*	Area (km^2)	(%)
Henley	JD	88	40
	PA	57	26
	PV	9	4
	PVO	66	30
	TOTAL	220	100
Nagle	B	53	6
	C-PD	94	11
	JD	90	10
	O-SN	329	37
	PP	287	32
	PV	25	3
	PVO	11	1
	TOTAL	888	100
Midmar	JD	414	45
	PA	82	9
	PE	28	3
	PES	148	16
	PVO	196	21
	TRT	57	6
	TOTAL	925	100
Albert Falls	JD	255	35
	PA	1	0
	PE	66	9
	PP	121	17
	PV	54	8
	PVO	224	31
	TOTAL	721	100
Inanda	B	586	44
	BM	12	1
	C-PD	138	10
	JD	68	5
	O-SN	195	15
	PP	248	19
	PV	60	5
	PVO	16	1
	TOTAL	1 322	100

* The symbols used are the same as those used in Table 2.3 (page 21)

A.2 Areal proportion of Mgeni impoundment catchments occupied by different land uses (Source: Umgeni Water)

HENLEY CATCHMENT

LANDUSE	AREA	
	(km^2)	(%)
Black transitional	8.26	3.76
CBD and industrial	0.31	0.14
Dams	0.56	0.26
Eucalyptus	6.46	2.94
Grassland	108.18	49.18
High density residential	0.25	0.11
Indigenous forest	11.70	5.32
Low density residential-gardens	44.04	20.02
Medium density residential-trees	0.89	0.40
Mix of undifferentiated forest	0.40	0.18
Other forest	0.31	0.14
Pines	4.08	1.86
Tree bush savannah	0.03	0.01
Undifferentiated cropping	26.82	12.20
Undifferentiated open spaces	3.90	1.77
Wetland	3.75	1.70
TOTAL	219.96	100.00

NAGLE CATCHMENT

LANDUSE	AREA (km^2)	(%)
Black transitional	12.15	1.37
CBD and industrial	2.25	0.25
Dams	1.44	0.16
Eucalyptus	68.31	7.69
Grasslands	55.28	6.22
High density residential	0.38	0.04
Indigenous forest	35.65	4.01
Irrigated pastures, crops	1.50	0.17
Low density residential-gardens	43.38	4.88
Low density smallholdings	5.73	0.65
Maize	64.36	7.24
Medium density residential-few trees	3.36	0.38
Medium density residential-trees	0.63	0.07
Mix of undifferentiated forest	8.38	0.94
Other cropping	0.19	0.02
Other forest	0.31	0.04
Parks, sports fields etc	0.66	0.07
Pines	80.55	9.07
Sugar cane	237.66	26.75
Tree bush savannah	82.66	9.30
Undifferentiated cropping	8.92	1.00
Undifferentiated open spaces	77.34	8.71
Valley of 1000 hills	33.51	3.77
Wattles	45.36	5.11
Woodland	18.46	2.08
TOTAL	888.40	100.00

MIDMAR CATCHMENT

LANDUSE	AREA (km^2)	(%)
Dams	19.69	2.12
Eucalyptus	19.52	2.11
Grassland	576.27	62.19
Indigenous forest	21.04	2.27
Irrigate pastures, crops	71.22	7.68
Low density residential-gardens	4.61	0.50
Low density smallholdings	10.68	1.15
Maize	48.49	5.23
Medium density residential-few trees	1.70	0.18
Medium density residential-trees	3.97	0.43
Mix of undifferentiated forests	5.68	0.61
Other cropping	2.34	0.25
Parks, sports fields, etc.	1.90	0.21
Pines	57.67	6.22
Private country schools	0.69	0.07
Sugar cane	2.63	0.28
Tree bush savanna	1.88	0.20
Undifferentiated cropping	43.90	4.74
Undifferentiated open spaces	10.49	1.13
Valley of 1000 hills	0.06	0.01
Wattles	9.25	1.00
Wetland	11.28	1.22
Woodland	1.63	0.18
TOTAL	926.57	100.00

ALBERT FALLS CATCHMENT

LANDUSE	AREA (km^2)	(%)
CBD and industrial	2.38	0.33
Dams	23.50	3.26
Eucalyptus	49.63	6.88
Grassland	199.39	27.64
Indigenous forest	49.36	6.84
Irrigated pastures, crops	24.55	3.40
Low density smallholdings	10.27	1.42
Maize	29.83	4.13
Medium density residential-few trees	6.46	0.90
Medium density residential-trees	5.40	0.75
Mix of undifferentiated forest	2.45	0.34
Other forest	2.31	0.32
Parks, sports fields, etc.	3.38	0.47
Pines	123.40	17.11
Sugar cane	23.28	3.23
Tree bush savanna	67.57	9.37
Undifferentiated cropping	43.65	6.05
Undifferentiated open spaces	27.81	3.86
Wattles	18.52	2.57
Woodland	8.17	1.13
TOTAL	721.30	100.00

INANDA CATCHMENT

LANDUSE	AREA	
	(km^2)	(%)
Black transitional	51.89	3.92
CBD and industrial	25.85	1.95
Dams	16.20	1.23
Eucalyptus	16.50	1.25
Grassland	143.33	10.84
High density residential	20.31	1.54
Indigenous forest	30.86	2.33
Irrigated pastures, crops	1.50	0.11
Low density residential-gardens	70.37	5.32
Low density smallholdings	17.39	1.31
Maize	32.46	2.46
Medium density residential-few trees	11.56	0.87
Medium density residential-trees	26.06	1.97
Mix of undifferentiated forest	22.80	1.72
Parks, sports fields, etc.	9.11	0.69
Pines	15.84	1.20
Sugar cane	119.98	9.70
Tree bush savannah	61.99	4.69
Undifferentiated cropping	58.16	4.40
Undifferentiated open spaces	35.09	2.65
Valley of 1000 hills	403.40	30.51
Wattles	9.27	0.70
Woodland	122.26	9.25
TOTAL	1322.18	100.00

APPENDIX B - METHODS OF SEDIMENT ANALYSIS, DATA MANIPULATION AND RESULTS

B.1 Analysis of bulk major and minor elemental composition

The major and minor elemental composition of the sediment was determined using X-ray fluorescence spectrometry.

B.1.1 Sample preparation

The air dried and ground samples were placed into a 105° C oven for 24hrs to ensure that the samples were completely dry. The dried samples were then crushed using a swing mill with a carbon steel vessel. The crushing time for each sample was approximately 1 minute, or until a fine powder had formed (-300#). Powder pellets and fusion discs were made for trace element and major element analyses, respectively (Duncan *et al*, 1984).

B.1.2 Analytical procedure

A Siemens SRS 303 AS XRF spectrometer, with a Rh tube was used for the analysis of the major elements and for the following trace elements - Mo, Nb, Zr, Y, Sr, U, Rb, Th, and Pb. A Philips PW1400 spectrometer with a tungsten (W) tube was used to determine Co, Cr, V and Mn. Zn, Cu, and Ni were analysed with the Philips spectrometer using a gold (Au) tube.

B.2 Identification of the clay minerals in the sediment samples

The clay minerals of the sediment samples were identified using the X-ray diffraction technique, after clay separation from the sediment matrix.

B.2.1 Clay separation and preparation for analysis

Approximately 100 g of a sediment was placed into a 250 ml plastic bottle. The bottle was filled with de-ionised water and shaken to form a slurry. The pH of the slurry was adjusted with drop-wise addition of 1M NaOH until it had stabilised at approximately 9. The pH-adjusted slurry was placed onto a reciprocal shaker overnight. The solution was then placed into a large plastic bucket and the volume of the bucket was made up with a pH 10 Na_2CO_3 solution. The contents of the bucket were then stirred vigorously and allowed to stand for approximately 16hrs. After that time period the supernatant, to a depth of approximately 18 cm, was siphoned into a separate bucket. The process of Na_2CO_3 addition, stirring, settling, and siphoning was continued a number times until sufficient clay had been separated for XRD analysis. Large quantities of NaCl were added to the slurry causing flocculation of the clay particles. Flocculation was enhanced by the drop-wise addition of 1M HCl, bringing the pH down to approximately 5. The flocculated material was placed into 50 ml centrifuge tubes and centrifuged at 6000 rpm for 5 minutes, disposing of the supernatant after each centrifuging stage.

The final clay concentrate slurry was placed into dialysis tubing. The dialysis tubing was first placed into a bucket with continuous water renewal and then into deionised water. Silver nitrate was used as an indicator to determine when all of the excess salt (chloride) had been removed from the sample. Once the salt had been removed an aliquot of the sample was taken and placed in a 105° C oven to determine the concentration of the clay in the slurry. The concentration of the slurry was adjusted to 10 mg/ml by the addition of de-ionised water.

The concentration adjusted slurry was pipetted onto a frosted glass slide. The slide was placed in a dry place away from any sources of contamination in order to dry the slurry. Care was taken not to dry the sample overly quickly to prevent the cracking of the clay layer.

again. This procedure was continued for 5 days to determine the effect that oxidation would have on the pH values.

B.4.1 Results of sediment pH (KCl) determination

Table B.4 pH of Mgeni catchment sediments after equilibration with 1M KCl (the trends are shown graphically in Figure 2.6)

Sample	pH (on successive days)				
	1	2	3	4	5
H	4.77	4.76	4.77	4.76	4.80
N1	5.54	5.02	5.14	4.68	4.85
N2	5.72	5.26	5.13	4.88	4.81
M1	5.15	5.00	4.84	4.80	4.71
M2	5.18	4.84	4.93	4.78	4.94
M3	5.08	5.24	5.23	5.24	5.28
AF	4.86	4.88	4.83	4.87	4.89
I1	5.63	6.62	5.61	5.62	5.62
I2	5.82	5.44	5.04	4.87	4.75
I3	6.41	6.06	5.83	5.71	5.63

B.5 P fractionation

To determine the distribution of P species in the sediment it was necessary to perform a sequential fractionation procedure. A number of such procedures have been reviewed in the literature (Pettersson *et al*, 1988; Furumai & Ohgaki, 1989; van Eck, 1982). The consensus of these reviews was that the technique suggested by Hieltjes & Lijklema (1980) was the most appropriate method, and that which could most easily be reproduced.

Hieltjes & Lijklema's (1980) method is a three stage extraction procedure. The first stage is an extraction with ammonium chloride (1M NH_4Cl, pH adjusted to 7) for two 30 minute periods, to determine the amount of exchangeable P. The second extraction is with sodium hydroxide (0.1M

NaOH) for 16 hours to determine the amount of non-apatite inorganic bound P. The final stage is with hydrochloric acid (0.5M HCl) for 24 hours to determine the amount of Ca bound P. In each case the sediment to extractant ratio was 2.5g:25ml. The sediment extractants were separated by centrifuging at 6000 rpm for 5 minutes and the extractants were then filtered through Whatman no. 1 filter paper. The Murphy & Riley (1962) colorimetric technique for P determination was used to analyse the extractant.

It was found that the second extraction stage could not be efficiently analysed by the Murphy & Riley (1962) technique. This is due to the high pH of the NaOH causing organic complexes and dispersed clay to come into solution, which interferes with P determination. As a consequence, only the exchangeable P concentrations are reported. The HCl extractions were not attempted because of the problems encountered with the NaOH extractions. Analyses were carried out in quadruplicate.

B.5.1 Results of P fractionation

Table B.5 Labile P in Mgeni catchment sediments (extracted with 1M NH_4Cl)

Sample	Labile P (ppm)
H	0.18
N1	0.42
N2	0.15
M1	0.27
M2	0.30
M3	0.27
AF	0.30
I1	0.42
I2	0.24
I3	0.81

B.6 Murphy & Riley P determination

The Murph & Riley (1962) method for the determination of P in natural waters is widely used. It is a colorimetric technique which relies on the fact that a solution containing P and molybdate will form a blue colour in the presence of antimony. This reaction is achieved through reacting a solution containing P with a mixed reagent which comprises sulphuric acid (5 N), ammonium molybdate, ascorbic acid (which is made up daily), and potassium antimonyl tartrate. The ratio of mixed reagent to sample is 4:21. The intensity of the blue colour which forms will depend on the concentration of P in the sample. The blue colour stabilises after 10 minutes and is stable for about 24 hours. Absorbance was read at a wavelength of 880 nm. Murphy & Riley (1962) suggest that a wavelength of between 800 and 882 nm is best for determining the absorbance of the molybdate-P blue colour. This was verified by determining the absorbance of a 2 µg/25 ml standard P solution over a variety of wavelengths. The results are plotted on Figure B.1.

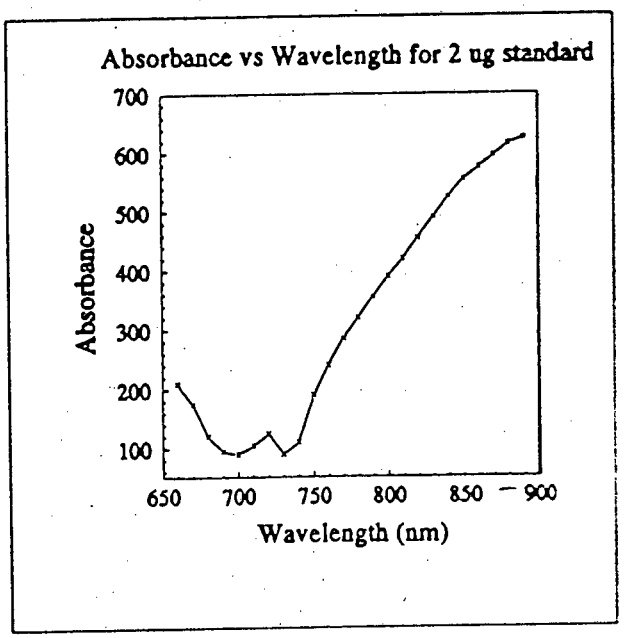


Figure B.1 Absorbance vs wavelength for 2 µg P standard

From these results it was decided that the optimum wavelength at which to take absorbance readings was 880 nm. The results of the absorbance readings were compared to those of standards (plotted on a 5 point calibration curve). Necessary care was taken to ensure that all the samples were diluted sufficiently to fall within the range of the standards. Duplicate analyses indicated that the method gives excellent reproducibility.

B.7 Particle size distribution (PSD) determination

The method described below is essentially that recommended by the Non-Affiliated Soil Analysis Work Committee (1990).

B.7.1 PSD analysis

B.7.1.1 Sample preparation

Prior to carrying out the PSD determination it was necessary to remove any cementing or flocculating agents that may be present in the sediment. Based on the nature of the material and the study area it was decided that organic matter and the iron oxides would necessarily be removed.

The removal of organic matter was facilitated by oxidising the material with hydrogen peroxide (H_2O_2). The sample was placed into a glass beaker which was then placed in a heated water bath. H_2O_2 was continually added until the sample no longer frothed with further addition. Heating was continued until most of the H_2O_2 had evaporated. The remaining sample was then centrifuged and placed into a 105° C oven overnight. The mass of the dried sample was measured and recorded.

The removal of iron oxide was promoted by the addition of a citrate-bicarbonate buffer to the H_2O_2 treated sample, to which 3 g of sodium dithionite ($Na_2S_2O_4$) was added. The sample was then placed into a pre-heated (80° C) water bath for 30 minutes. The sample was then removed and centrifuged. The supernatant was discarded. The sample was then centrifuged and washed with de-ionised water, dried at 105° C overnight, and weighed.

B.7.1.2 PSD determination : Pipette method

The pre-treated oven dried soil was placed into a 250 ml bottle, containing 10 ml of Calgon solution. The volume of the bottle was made up to 150 ml with de-ionised water and the bottle was placed onto a reciprocal shaker overnight. Calgon addition and shaking was carried out to ensure the complete dispersion of the sample.

The dispersed sample was transferred to a 1 l cylinder and the volume was made up to the 1000 ml mark with de-ionised water. The suspension was stirred with a hand stirrer for 1 minute, the time when stirring stopped was recorded. A Lowy pipette was lowered into the suspension to a depth determined by the ambient temperature and the size fraction which was being determined (as relates to Stoke's Law), Table B.6.

Table B.6 Times and depths at which size fractions were withdrawn

Temperature	0.05 mm (coarse silt)	0.02 mm (fine silt)	0.002 mm (clay)
° C	15 cm depth	10 cm depth	10 cm depth
20	40 seconds	4 minutes 39 seconds	7 hours 45 minutes

A 25 ml sample was drawn at each depth and emptied into a tared crucible which was placed into a 105°C oven overnight. The mass of the dried sample was determined and recorded.

The sand fraction of the sediment was determined by washing the remaining suspension, after pipetting, through a 0.053 mm sieve and drying the sediment retained on the sieve (105° C overnight) and weighing.

B.7.2 PSD results

Table B.7 Particle size distribution of Mgeni catchment sediments

Sample	Clay %	Silt %	Sand %
H	58.43	38.96	2.61
N1	88.24	11.76	0.00
N2	68.40	12.67	18.93
M1	63.33	36.67	0.00
M2	55.17	43.25	1.47
M3	42.72	14.24	43.04
AF	51.48	21.06	27.46
I1	70.75	24.61	4.64
I2	88.24	11.76	0.00
I3	91.89	8.11	0.00

The results have been normalised to 100%.

B.8 Surface area determination

The surface areas of the Inanda samples were determined in the Particle Technology Centre, in the Chemical Engineering Department of the University of Cape Town. The analyses were carried out on a Micrometrics ASAP 2000 machine, using nitrogen as the analysis gas.

Table B.8 Summarised results of surface area determinations of Inanda samples

Sample	BET surface area (m^2/g)	Single Point surface area (m^2/g)	Average pore diameter (Å)
I1	30.8	29.2	111.2
I2	51.7	49.1	115.4
I3	59.7	56.7	116.0

B.9 pH, E.C. and REDOX potential measurements

All pH measurements were made on a Crison Micro pH 2001 meter. The probe was calibrated to pH 7.02 and pH 4.00. Electrical conductivity measurements were taken on a Crison CM 2201 meter. All REDOX potential measurements were taken with a Corning 255 Ion analyzer, using a platinum REDOX combination electrode.

APPENDIX C - DATA MANIPULATION AND RESULTS OF P SORPTION EXPERIMENTAL WORK

C.1 P sorption

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
H	5.69	0.00	0.00
	5.72	0.00	0.00
	5.68	0.00	0.00
	5.64	0.00	0.00
	5.64	0.00	0.00
	5.68	0.00	0.00
	5.70	0.00	0.00
	5.59	0.03	0.34
	5.77	0.06	0.64
	5.78	0.28	2.82
	5.77	3.37	33.71
N1	5.10	0.01	0.00
	5.42	0.03	0.33
	5.44	0.01	0.07
	5.46	0.02	0.19
	5.54	0.01	0.05
	5.13	0.00	0.05
	5.52	0.02	0.17
	5.43	0.04	0.40
	5.70	0.17	1.73
	5.74	0.88	8.81
	5.82	1.99	19.86
N2	5.51	0.02	0.00
	5.45	0.00	0.00
	5.57	0.00	0.00
	5.59	0.00	0.00
	5.57	0.01	0.10
	5.54	0.01	0.08
	5.57	0.03	0.26
	5.56	0.03	0.30
	5.50	0.16	1.57
	5.80	0.86	8.63
	5.78	1.49	14.90
M1	5.18	0.03	0.26
	4.70	0.01	0.09
	5.56	0.02	0.21
	5.59	0.01	0.08
	4.93	0.00	0.03
	5.33	0.01	0.09
	5.40	0.01	0.06
	5.37	0.03	0.28
	5.55	0.12	1.25
	5.63	0.66	6.59
	5.45	0.73	7.31

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
M2	5.46	0.00	0.00
	5.58	0.00	0.00
	5.47	0.00	0.00
	5.61	0.00	0.00
	5.61	0.00	0.04
	5.54	0.00	0.00
	5.66	0.01	0.11
	5.63	0.08	0.78
	5.67	0.60	6.00
	5.57	3.90	39.01
	5.62	5.17	51.74
M3	6.15	0.01	0.00
	6.18	0.01	0.08
	6.27	0.00	0.00
	6.18	0.01	0.15
	6.17	0.00	0.00
	6.20	0.00	0.00
	6.15	0.01	0.13
	6.14	0.14	1.44
	6.19	1.10	10.96
	6.13	4.22	42.21
	6.17	7.40	74.00
AF	5.79	0.02	0.00
	5.89	0.01	0.06
	6.07	0.01	0.13
	6.08	0.01	0.09
	5.88	0.01	0.14
	6.12	0.01	0.14
	5.74	0.02	0.20
	5.58	0.09	0.87
	5.90	0.78	7.82
	5.69	2.64	26.37
	5.87	5.99	59.94
I1	6.43	0.02	0.18
	6.43	0.00	0.04
	6.55	0.01	0.11
	6.46	0.02	0.18
	6.41	0.01	0.11
	6.40	0.01	0.11
	6.36	0.01	0.15
	6.39	0.25	2.48
	6.37	1.59	15.90
	6.35	5.15	51.54
	6.22	7.92	79.21

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
I2	4.98	0.00	0.00
	4.94	0.00	0.00
	4.95	0.00	0.00
	4.97	0.00	0.00
	5.00	0.01	0.10
	5.04	0.01	0.08
	4.49	0.03	0.26
	4.95	0.03	0.30
	4.91	0.16	1.57
	5.06	0.86	8.63
	5.06	1.49	14.90
I3	5.99	0.00	0.04
	6.05	0.01	0.13
	6.06	0.02	0.21
	6.13	0.03	0.32
	6.17	0.03	0.28
	6.36	0.03	0.30
	6.15	0.05	0.45
	6.15	0.05	0.54
	6.09	0.25	2.55
	6.14	1.26	12.63
	6.10	1.70	16.97

C.2 P sorption at different pH conditions

(including Figure C.1 - P sorption isotherms for the pH dependent sorption experiments)

Appendix C (Part 2)

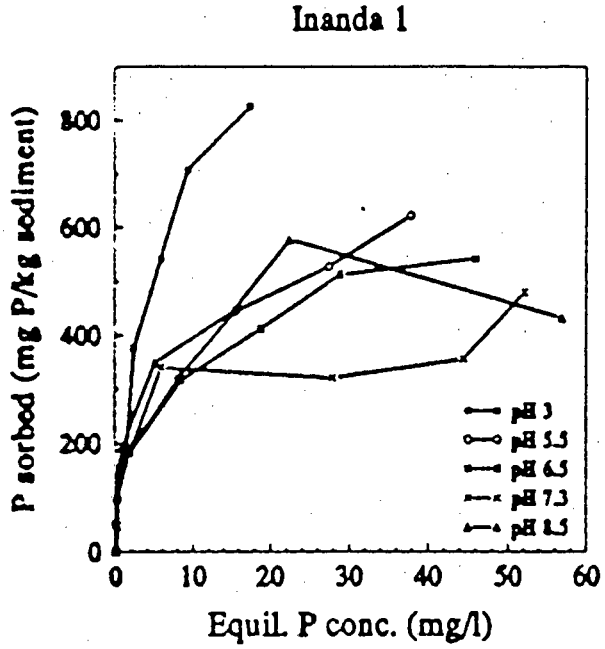
Sample Equil. pH	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
I1	2.88	0.02	0.00
pH 3	2.75	0.11	1.45
	2.72	0.05	49.50
	2.89	0.19	98.08
	2.88	1.45	185.51
	2.97	2.35	376.53
	3.13	5.87	541.33
	3.05	9.35	706.51
	3.12	17.42	825.79
I1	5.41	0.02	0.00
pH 5.5	5.43	0.12	1.26
	5.56	0.01	49.86
	5.47	0.21	97.89
	5.46	1.69	183.13
	5.39	8.07	319.29
	5.4	15.59	444.10
	5.6	27.33	526.72
	5.58	37.79	622.15
I1	6.37	0.00	0.00
pH 6.5	6.42	0.00	2.50
	6.43	0.00	50.00
	6.72	0.28	97.16
	6.56	1.82	181.84
	6.69	8.40	315.99
	6.53	18.80	411.99
	6.57	28.80	512.04
	6.47	45.86	541.43
I1	7.18	0.17	0.00
pH 7.3	7.25	0.22	0.30
	7.3	0.32	46.79
	7.28	0.28	97.16
	7.34	1.74	182.58
	7.34	5.93	340.71
	7.38	27.88	321.22
	7.4	44.39	356.11
	7.35	52.09	479.12
I1	8.5	0.02	0.00
pH 8.5	8.42	0.03	2.23
	8.45	0.02	49.77
	8.49	0.15	98.54
	8.53	0.86	191.38
	8.56	5.07	349.27
	8.57	15.40	445.97
	8.55	22.38	576.25
	8.63	56.86	431.42

Appendix C (Part 2)

Sample Equil. pH	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
I2	2.32	0.05	0.00
pH 2.5	2.54	0.04	2.09
	2.62	0.05	49.51
	2.59	0.11	98.93
	2.5	0.28	197.19
	2.52	1.00	389.96
	2.61	3.70	563.02
	2.37	4.00	759.98
	2.56	8.42	915.85
I2	3.5	0.01	0.00
pH 3.5	3.46	0.02	2.31
	3.45	0.06	49.38
	3.47	0.10	99.02
	3.42	0.35	196.51
	3.41	1.07	389.28
	3.46	4.89	551.14
	3.47	7.23	727.73
	3.49	9.77	902.28
I2	6.36	0.14	0.00
pH 6.2	6.17	0.08	1.71
	6.48	0.17	48.25
	6.36	0.23	97.66
	6.43	0.42	195.83
	6.09	2.67	373.33
	6.25	5.65	543.50
	6.28	22.84	571.59
	6.11	11.30	887.00
I2	7.12	0.01	0.00
pH 7.3	7.44	0.03	2.18
	7.57	0.03	49.72
	7.36	0.07	99.27
	7.34	0.30	197.02
	7.35	1.28	387.24
	7.36	4.38	556.23
	7.34	6.21	737.92
	7.45	10.45	895.49
I2	7.94	0.00	0.00
pH 8.0	7.97	0.00	2.50
	8.05	0.00	50.00
	8.11	0.12	98.76
	8.16	0.57	194.30
	7.99	2.84	371.63
	8.15	11.08	489.19
	8.1	31.84	481.64
	7.99	33.32	666.77

Appendix C (Part 2)

Sample Equil. pH	pH	Equil. conc. ug/ml	mg P sorbed/kg sediment
I3	4.07	0.02	0.00
pH 3.8	3.81	0.02	2.26
	3.84	0.04	49.64
	3.75	0.02	99.78
	3.77	0.15	198.54
	3.85	0.53	394.71
	3.77	1.28	587.23
	3.87	1.80	782.04
	3.85	3.69	963.12
I3	5.4	0.01	0.00
pH 5.2	5.36	0.00	2.50
	5.29	0.00	50.00
	5.32	0.00	100.00
	5.37	0.15	198.54
	5.21	1.17	388.26
	5.18	4.16	558.37
	5.23	8.25	717.55
	5.12	7.91	920.94
I3	7.12	0.00	0.00
pH 7.2	7.1	0.00	2.50
	7.24	0.00	50.00
	7.19	0.00	100.00
	7.2	0.18	198.20
	7.23	1.48	385.21
	7.14	4.73	552.72
	7.33	6.89	731.13
	7.07	15.88	841.18
I3	7.91	0.02	0.00
pH 8.1	7.93	0.01	2.43
	8.01	0.04	49.64
	8.08	0.03	99.70
	8.1	0.09	199.05
	7.96	0.63	393.69
	8.02	2.64	573.65
	8.25	9.26	707.37
	7.93	17.17	828.31
I3	8.52	0.06	0.00
pH 8.7	8.62	0.03	2.22
	8.78	0.03	49.68
	8.64	0.02	99.78
	8.64	0.21	197.86
	8.67	0.46	395.39
	8.63	3.71	562.90
	8.99	12.49	675.12
	8.52	16.83	831.70



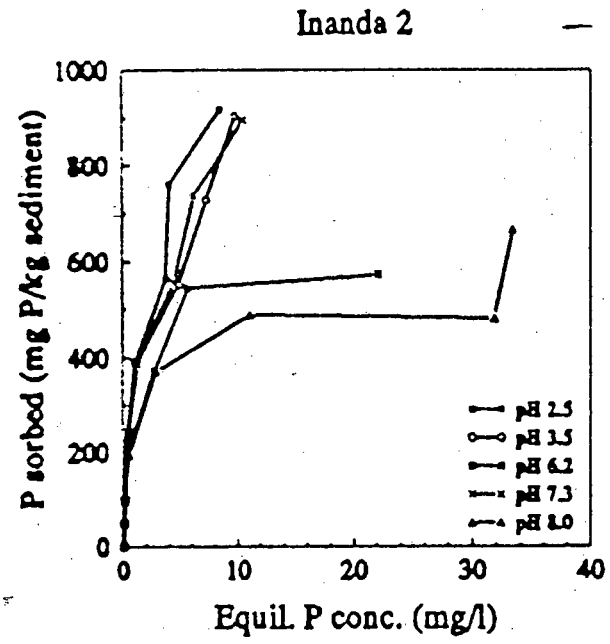


Figure C.1 Sorption isotherms showing the relationship between P sorption and pH

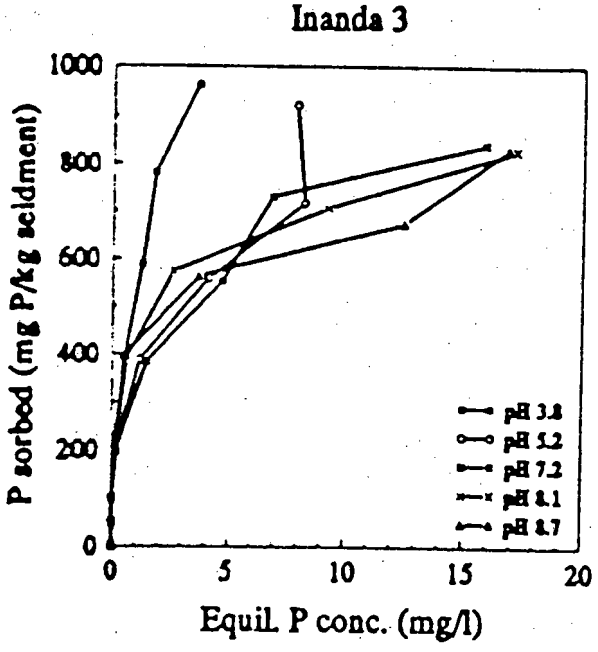


Figure C.1 (cont.) Sorption isotherm showing the relationship between P sorption and pH

C.3 P sorption at different redox conditions

Appendix C (Part 3)

Sample	Eh mV	pH	Equil. conc ug/ml	mg P sorbed/kg sediment
I1	113.6	4.68	0.53	399.41
	180.0	4.48	0.05	410.44
	208.2	4.67	0.17	418.85
	189.6	4.83	0.00	421.21
	204.4	5.07	0.07	425.66
	233.1	4.94	0.00	431.44
	243.3	4.93	0.08	434.52
	241.2	4.66	0.10	439.38
	237.7	4.86	0.01	445.57
I2	117.4	4.65	0.11	397.19
	139.3	4.65	0.02	410.06
	192.7	4.55	0.05	418.02
	190.0	4.62	0.06	432.60
	260.5	4.51	0.01	430.90
	287.4	4.48	0.01	442.53
	254.6	4.47	0.01	451.07
	278.9	4.23	0.00	455.28
	248.5	4.42	0.01	464.96
I3	64.0	5.19	0.07	395.06
	87.3	5.18	0.02	402.94
	99.0	5.24	0.04	413.99
	126.0	5.18	0.05	420.52
	153.4	5.29	0.01	433.55
	168.8	5.34	0.00	435.29
	192.5	5.22	0.00	442.95
	212.7	5.04	0.00	449.58
	202.2	5.16	0.00	456.27

C.4 P desorption

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P desorbed/kg sediment
H	5.69	0.00	0.00
	5.72	0.00	0.00
	5.68	0.00	0.00
	5.64	0.00	0.00
	5.64	0.00	0.00
	5.68	0.00	0.00
	5.70	0.00	0.00
	5.59	0.03	0.34
	5.77	0.06	0.64
	5.78	0.28	2.82
	5.77	3.37	33.71
N1	5.10	0.01	0.00
	5.42	0.03	0.33
	5.44	0.01	0.07
	5.46	0.02	0.19
	5.54	0.01	0.05
	5.13	0.00	0.05
	5.52	0.02	0.17
	5.43	0.04	0.40
	5.70	0.17	1.73
	5.74	0.88	8.81
	5.82	1.99	19.86
N2	5.51	0.02	0.00
	5.45	0.00	0.00
	5.57	0.00	0.00
	5.59	0.00	0.00
	5.57	0.01	0.10
	5.54	0.01	0.08
	5.57	0.03	0.26
	5.56	0.03	0.30
	5.50	0.16	1.57
	5.80	0.86	8.63
	5.78	1.49	14.90
M1	5.18	0.03	0.26
	4.70	0.01	0.09
	5.56	0.02	0.21
	5.59	0.01	0.08
	4.93	0.00	0.03
	5.33	0.01	0.09
	5.40	0.01	0.06
	5.37	0.03	0.28
	5.55	0.12	1.25
	5.63	0.66	6.59
	5.45	0.73	7.31

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P desorbed/kg sediment
M2	5.46	0.00	0.00
	5.58	0.00	0.00
	5.47	0.00	0.00
	5.61	0.00	0.00
	5.61	0.00	0.04
	5.54	0.00	0.00
	5.66	0.01	0.11
	5.63	0.08	0.78
	5.67	0.60	6.00
	5.57	3.90	39.01
	5.62	5.17	51.74
M3	6.15	0.01	0.00
	6.18	0.01	0.08
	6.27	0.00	0.00
	6.18	0.01	0.15
	6.17	0.00	0.00
	6.20	0.00	0.00
	6.15	0.01	0.13
	6.14	0.14	1.44
	6.19	1.10	10.96
	6.13	4.22	42.21
	6.17	7.40	74.00
AF	5.79	0.02	0.00
	5.89	0.01	0.06
	6.07	0.01	0.13
	6.08	0.01	0.09
	5.88	0.01	0.14
	6.12	0.01	0.14
	5.74	0.02	0.20
	5.58	0.09	0.87
	5.90	0.78	7.82
	5.69	2.64	26.37
	5.87	5.99	59.94
I1	6.43	0.02	0.18
	6.43	0.00	0.04
	6.55	0.01	0.11
	6.46	0.02	0.18
	6.41	0.01	0.11
	6.40	0.01	0.11
	6.36	0.01	0.15
	6.39	0.25	2.48
	6.37	1.59	15.90
	6.35	5.15	51.54
	6.22	7.92	79.21

Appendix C (Part 4)

Sample	pH	Equil. conc. ug/ml	mg P desorbed/kg sediment
I2	4.98	0.00	0.00
	4.94	0.00	0.00
	4.95	0.00	0.00
	4.97	0.00	0.00
	5.00	0.01	0.10
	5.04	0.01	0.08
	4.49	0.03	0.26
	4.95	0.03	0.30
	4.91	0.16	1.57
	5.06	0.86	8.63
	5.06	1.49	14.90
I3	5.99	0.00	0.04
	6.05	0.01	0.13
	6.06	0.02	0.21
	6.13	0.03	0.32
	6.17	0.03	0.28
	6.36	0.03	0.30
	6.15	0.05	0.45
	6.15	0.05	0.54
	6.09	0.25	2.55
	6.14	1.26	12.63
	6.10	1.70	16.97