

**THE PHOSPHORUS SORPTION
BEHAVIOUR OF SOME SOUTH AFRICAN WATER
TREATMENT RESIDUES**

BY

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PREFACE

The experimental work described in this thesis was carried out in the School of Environmental Sciences, University of Kwa-Zulu Natal, Pietermaritzburg, from January 2009 to November 2009, under the supervision of Dr Louis Titshall.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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ABSTRACT

Water treatment residues (WTRs), which are by-products from the production of potable water, are chemically benign, inorganic materials which are suitable for disposal by land application. Their high phosphorus (P) sorption capacities have, however, generated some concern in an agronomic context where P is recognised as a growth limiting plant nutrient. The extent to which labile P pools are reduced or enhanced by WTR amendments is, therefore, a central issue with respect to their disposal by land application. Therefore, the aim of this study was, through the use of empirical adsorption isotherm equations and chemical fractionation of P within the residues, to investigate the chemical processes responsible for the retention and release of P from 15 South African WTRs.

Chemical characterisation revealed considerable variation in residue properties relevant to P sorption-desorption processes. pH, exchangeable Ca and organic carbon content ranged from 4.77 to 8.37, 238 to 8 980 mg kg⁻¹ and 0.50 to 11.6 %, respectively. Dithionate, oxalate and pyrophosphate extractable Al fractions ranged from 741 to 96 375, 1 980 to 82 947 and 130 to 37 200 mg kg⁻¹, respectively. Dithionate, oxalate and pyrophosphate extractable Fe ranged from 441 to 15 288, 3 865 to 140 569 and 230 to 90 000 mg kg⁻¹ respectively. Therefore mechanisms of retention were hypothesised to be residue specific, being dependent on the unique chemical properties of the sorbent. Elevated Ca and amorphous Al and Fe concentrations did, nevertheless, suggest that all residues had the capacity to adsorb high amounts of P and to retain this P in forms unavailable for plant uptake. These arguments were confirmed by the sorption study where labile P was, for all residues, found to constitute a small fraction of total applied P even at high application concentrations (128 mg P L⁻¹). Sequential P fractionation revealed that most of the inherent P (which ranged from 1 149 to 1 727 mg P kg⁻¹) and applied P were retained in highly resistant mineral phases or fixed within the organic component. Thus P replenishment capacities were restricted even though residual P concentrations were often within adequate ranges for plant growth.

Phosphorus adsorption data was described by four empirical adsorption isotherm equations in an effort to determine possible mechanisms of retention. Sorption data was, for most of the WTRs, described by the Temkin isotherm while the Freundlich and linear models fitted data for two residues each. A key finding was that the distribution coefficient (K_d) tended to increase with the quantity of P adsorbed (S) as opposed to decrease or remain constant in accordance with model assumptions. Therefore, the models could not be used for mechanistic interpretation, even though

they provided excellent descriptions of the data. The direct relationship between K_d and S suggested a mechanism of retention involving the activation of sorption sites. This notion was supported by the fractionation study which showed that P addition results in the transfer of an increasing quantity of organically bound P to resistant residual forms. Model affinity parameters were strongly correlated to dithionate and pyrophosphate extractable Al and Fe which suggested that P was adsorbed primarily through ligand exchange mechanisms. The mobility of P bound to organic fractions did indicate that P was retained through weaker forces of attraction such as monodentate ligand exchange, charge neutralisation or proton transfer. Evidence to support the notion that P is immobilised through the formation of Ca phosphates was lacking.

Based on P fractionation data, it was suggested that strong chemisorption mechanisms and the diffusion of P into WTR micropores were largely responsible for the minimal quantity of P desorbed by disequilibria desorption processes. A greater quantity of P was desorbed in the presence of oxalate and citrate which suggested that plants may increase bio-available pools through the release of organic ligands. Phosphorus desorbed in the presence of these ligands did, however, decline with P addition which confirmed that the affinity of the WTR surface for P increases with P application. Therefore, it was concluded that the application of P to WTRs is an uneconomical process unless sorption sites are already saturated or immobilisation processes are inhibited. In light of these findings, it was suggested that the absence of plant P deficiencies under the field application of WTRs is due primarily to inhibited sorption.

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INTRODUCTION

Water treatment residues (WTRs) are by-products from the production of potable water and have been defined as “the accumulated solids or precipitate removed from a sedimentation basin, settling tank, or clarifier in a water treatment plant” (Hughes *et al.*, 2007). These residues are comprised of mineral and humic material that is removed and precipitated from the raw water, together with the residues of any treatment chemicals used as flocculants and coagulants (commonly aluminium or iron salts) and coagulant aids (mostly organic polymers) (Babatunde and Zhao, 2007). In the United States of America, more than 2 million metric tons of WTR are generated daily (Prakash and Sengupta, 2003) while South Africa produces over 5 million cubic meters of wet WTR per annum (Hughes *et al.*, 2005). Babatunde and Zhao (2007) have estimated that on a global scale 10 000 tons of WTR (as dry solids) is produced daily.

Water treatment residues have traditionally been disposed of to landfill, at great expense to municipalities, stored in on-site lagoons or discharged directly into watercourses or sewer systems (Dayton, 1995). In recent years the combination of rising disposal costs, increasingly stringent environmental legislation and an ever-increasing demand for clean water (with a concomitant increase in residue production) has stimulated research into alternative forms of disposal. Forthcoming solutions have been varied with WTRs finding uses in the building and construction industry (Babatunde and Zhao, 2007), as a component of broiler litter (Maurice *et al.*, 1998) and as soil substitutes (Dayton and Basta, 2001). Land-based systems have become especially popular for the final disposal of WTRs and numerous studies have focused on the uses of these residues in agricultural and environmental contexts. Land application is an appealing disposal alternative as it constitutes an open system offering potential for waste treatment rather than simply waste disposal such as is associated with landfill (Titshall and Hughes, 2005). Furthermore, it has been suggested, on the basis of numerous studies (Elliott *et al.*, 1990b; Geertsema *et al.*, 1994; Hughes *et al.*, 2007), that the physical and chemical properties of WTRs make them suitable for use as a soil ameliorant or amendment.

An aspect regarding the land application of WTRs which has generated considerable debate has been their effect on soil phosphorus (P) chemistry. Although variable in composition, WTRs commonly contain substantial quantities of amorphous iron (Fe) and aluminium (Al) hydrous-oxides which are strong adsorbents of inorganic P. Ippolito *et al.* (2003) found that the P sorption capacity

of an Al based WTR was 12 500 mg P kg⁻¹ after 24 hours equilibration time. Although P sorption capacities are highly variable and often lower than reported by Ippolito *et al.* (2003), several studies have confirmed sorption capacities greater than 7 000 mg P kg⁻¹ (Dayton, 1995; Makris *et al.*, 2004a; Makris *et al.*, 2005). This high P sorption potential has been viewed as either beneficial or problematic depending on the context in which the WTR is to be used.

In soils where P concentrations are over the P adsorption capacity of that soil, the ability of soil-applied WTR to adsorb, as well as retain, excess P has been considered a beneficial property as it limits excess P contamination of surrounding environments. Numerous studies (Macks *et al.*, 1998; Haustein *et al.*, 2000; Agyin-Birikorang *et al.*, 2008) have demonstrated the potential of WTRs to act as ‘eutrophication preventatives’ by reducing the quantity of P in surface runoff to within environmentally acceptable limits. For example, Elliot *et al.* (2002) found that a calcium based WTR dramatically reduced soluble P concentrations in soils that were treated with P-rich biosolids and fertilizer. The utilisation of WTRs in this manner is a low-cost alternative to mitigate P pollution from P-rich soils (Babatunde and Zhao, 2007), as well as presenting an alternative method of disposing of WTR.

Conversely, in an agronomic context, the high P sorption capacities of WTRs have been viewed as problematic due to the potential of the WTR to induce plant P deficiencies. The extent and consequences of these deficiencies have been demonstrated by numerous studies, many of which are based on pot experiments. For example, Hyde and Morris (2000) concluded that optimum P concentrations on agricultural land could be rapidly reduced by the application of WTR. Cox *et al.* (1997) found that dry biomass of wheat and P uptake by the wheat were significantly reduced when grown on a WTR amended soil. While these studies suggest that P deficiencies may restrict the agricultural utilisation of WTRs, observed negative effects are generally restricted to pot experiments. Studies involving field trials (Elliott *et al.*, 1990a; Basta, 2000; Hughes *et al.*, 2005) have demonstrated that detrimental effects on plant P uptake are limited even at very high WTR application rates. It has been noted that under field conditions, WTRs may contribute to crop P-nutrition as the residue decomposes with time (Ahmed *et al.*, 1997; Hughes *et al.*, 2005).

While the contradictory findings between field and laboratory based data have been attributed to factors such as unrealistic plant populations and nutrient imbalances, often associated with pot experiments, (Hughes *et al.*, 2005), factors affecting the chemical processes involved in the retention

(sorption) and release (desorption) of P by WTRs have not been widely researched. Most studies considering the land application of WTRs have examined the magnitude and subsequent effects (e.g. induced plant P deficiencies; Bugbee and Frink, 1985; reductions in the loss of excess P to surface waters; Agyin-Birikorang *et al.*, 2008) of P sorption by WTR amended soils. However, comparatively few studies (Butkus *et al.*, 1998, Makris *et al.*, 2004b, Yang *et al.*, 2006) have focussed on the specific sorption mechanisms of WTRs and their affects on P speciation and availability. Insight into the nature of these processes is essential in a land application context if WTRs are to be disposed of effectively.

The overall aim of this study is to gain insight into the nature of the chemical processes responsible for the retention and release of P from a range of South African WTRs. The study will, more specifically, investigate the mechanisms and chemical processes involved in the adsorption and desorption of P from these residues. Furthermore the chemical properties of these residues, which are relevant to sorption desorption processes, are characterised. Recommendations and suggestions, based on the findings from this study, are made that may improve the efficiency of land application in both agronomic and environmental contexts. It should be noted that the terms ‘WTR’ and ‘residue’ are synonymously to refer to water treatment residue.

The dissertation is divided as follows:

- Chapter 1 reviews current knowledge on the P sorption and desorption behaviour of WTRs.
- Chapter 2 involves the chemical characterisation and phosphorus fractionation of 15 South African WTRs.
- Chapter 3 examines the phosphorus sorption behaviour of 15 South African WTRs. Adsorption processes are quantified through the use of empirical adsorption isotherm equations and the chemical fractionation of adsorbed P.
- Chapter 4 focuses on the mechanisms responsible for the desorption of P from 15 untreated and 7 P-treated South African WTRs.
- Chapter 5 provides an overview of the major findings from the study and suggests areas that require further research.

CHAPTER 1

PHOSPHORUS SORPTION BEHAVIOUR OF WATER TREATMENT RESIDUES: A REVIEW

1.1 Introduction

The utilisation of land for waste disposal purposes has received considerable attention over the last decade due to the environmental and economic concerns surrounding more traditional forms of disposal such as land-fill and incineration. Land disposal presents an appealing alternative to conventional disposal as it suggests that wastes can be assimilated without inducing negative effects on soil quality, groundwater or plant growth (Titshall and Hughes, 2005). Furthermore, land disposal systems may be engineered to favourably modify soil properties and beneficially recycle waste components (Elliott *et al.*, 1990a). This implies that this form of disposal is particularly suitable with ameliorative properties (e.g. liming potential) and low toxicity. One such group of wastes are water treatment residues (WTRs) which have been defined as the accumulated solids or precipitates removed from a sedimentation basin, settling tank, or clarifier in a water treatment plant (Herselman, unpublished).

The land application of WTRs has been shown to have a number of beneficial effects on soil organic carbon, soil structure and water holding capacity (Rengasamy *et al.*, 1980; Geertsema *et al.*, 1994; Zupancic, 1996; Hughes *et al.*, 2005). There is, however, concern regarding the high P sorption capacities of WTRs and the potential negative effects of their application to soil on plant available P. Ippolito *et al.* (2003) noted that, from an agricultural perspective, the single greatest disadvantage of WTR is the adsorption of plant available soil-P. In a study on P availability in WTR amended soils, Hyde and Morris (2000) concluded that above optimal P concentrations on agricultural land could be rapidly reduced by the application of WTRs. Bugbee and Frink (1985) found that the growth of lettuce (*Lactuca sativa* cv. Iceberg) and marigolds (*Tagetes* cv. Lemon-drop) were significantly restricted due to phosphorus deficiency when grown on WTR treated soil. Deficiencies were evident at relatively low alum WTR application rates (5 % by volume) and could not be overcome by doubling the initial P fertiliser rate. While numerous other studies have observed similar results (Dayton, 1995; Cox *et al.*, 1997; Wang *et al.*, 1998), Hughes *et al.* (2005) suggest that such effects may be exaggerated in pot experiments due to nutrient imbalances and unrealistic plant populations.

Phosphorus is essential for all forms of life because of its role in ribonucleic acid and function in energy transfers via adenosine tri-phosphate (Ozanne, 1980). A soil solution P concentration of 0.20 mg P L^{-1} is often reported as the optimum value for plant growth, though this varies depending on the plant species (Sims and Pierzynski, 2005). Silver grass (*Miscanthus sinensis*), for example, attains a maximum yield at only 0.03 mg P L^{-1} while flatweed (*Hypochoeris radicala*) requires a solution concentration of 0.76 mg P L^{-1} (Ozanne, 1980). Maintenance of optimal solution P concentrations (commonly achieved through the addition of P fertiliser) is therefore crucial to agricultural productivity. In an effort to achieve maximum crop yield, P fertilisers are often over applied resulting in the excessive loss of P to surface waters. Once P concentrations in surface waters exceed 0.35 mg P L^{-1} , the excessive growth of algae and aquatic weeds result in eutrophication (Bundy *et al.*, 2005).

Eutrophication is of environmental concern due to its detrimental impact on surface water quality. In addition to correct agricultural management practices, the application of materials with high P sorption capacities such as WTRs, has been viewed as a means to control the loss of excess P (Haustein *et al.*, 2000). Agyin-Birikorang *et al.* (2008) concluded that the land application of WTR could effectively reduce offsite P transport to nutrient-sensitive surface water systems. Soluble P values measured in WTR amended plots were significantly lower than in non-amended plots after hurricane induced flooding. In studies conducted by Gallimore *et al.* (1999) and Haustein *et al.* (2000), WTRs were found to be effective at inhibiting runoff-P. In this study adsorption efficacy was found to be a function of the WTRs chemical properties, specifically Al content. Water treatment residues have also been found to be effective at controlling P losses when co-applied with organic P sources (Oladeji *et al.*, 2008) and at removing P from contaminated waters (Macks *et al.*, 1998). Thus, while seen as a liability in certain agricultural land application contexts, the P sorption capacity of WTRs is viewed as a useful characteristic in applications where mitigation of P induced eutrophication is the focus.

Elliott *et al.* (1990a) noted that the difficulties associated with the land application of WTRs, particularly those pertaining to a decline in available P, tend to be qualitatively different from those associated with wastes such as sewage sludges. High concentrations of heavy metals will lower the potential of a soil for agricultural production while the presence of pathogens may limit the use of crops grown for human consumption, two issues often associated with sewage sludges. However, a decrease in plant available P suggests that fertilizer may have to be applied to obtain the optimal

crop productivity. Conversely, in an environmental context, higher rates of application of WTR may be required to reduce soil solution P to within acceptable environmental limits. These are management problems and the solutions for them will invariably involve specific management strategies such as appropriate crop selection or the application of additional P-fertilizer or additional residue. Effective implementation of such strategies does, however, require insight into the mechanistic nature of the processes involved. In terms of WTR-P relations, this suggests:

1. an understanding of which mechanisms are operative in terms of the sorption of P by WTRs and the desorption of P from WTRs, and
2. an understanding of the extent to which these mechanisms are influenced by characteristics (e.g. chemical composition, pH) and field variables (e.g. soil texture, moisture content).

Ultimately application efficiency, whether it be from an agricultural or environmental perspective, can only be maximised if the micro-processes are recognised.

This review examines current knowledge on the P sorption and desorption behaviour of WTRs. This chapter will provide an overview of the major P sorption and desorption mechanisms occurring at the water treatment residue surface-solution interface, including consideration of some of the common models used to describe these processes. The processes involved are reviewed in both agronomic and environmental contexts.

1.2 Characteristics of Water Treatment Residues

1.2.1 Origins of Water Treatment Residues

The production of potable water from turbid primary sources requires the removal of suspended and dissolved solids, organic matter and other contaminants from the raw water source (Hughes *et al.*, 2005). This is achieved through the addition of treatment chemicals which isolate unwanted constituents through flocculation and coagulation processes. The physical and chemical characteristics of the resulting residues depend largely on the characteristics of the raw water source, the coagulant type used and dosage applied and other relevant, but plant-specific, operating conditions (Babatunde and Zhao, 2007). In their report on the land application of WTRs, Hughes *et al.* (2005) preferred the use of the term ‘residue’ over the term ‘sludge’, arguing that the latter term had too many negative connotations associated with sewage-sludge. This is a noteworthy distinction in the context of land application given the benign nature of the majority of these residues.

Water treatment residues have been classified as either coagulant, lime or softening, natural or manganese residues with coagulant and softening residues representing the majority of residues (approximately 70 % and 25 % respectively) (Babatunde and Zhao, 2007; Herselman, unpublished). Coagulant residues are formed when alum salts ($\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$), ferric salts (FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$) and organic polymers are added to water. These materials act as effective coagulants by destabilising dispersed particles, providing new particles that accelerate the rate of particle collision and thus aggregation and by acting as strong adsorbents of dissolved organic materials and many trace contaminants (Elliott *et al.*, 1990a). Softening residues are comprised primarily of calcium and magnesium carbonates which are formed when lime, sodium hydroxide and/or soda ash are used to treat hard or alkaline water. Some plants may also add organic polymer or metal salts to remove fine precipitates, colour or turbidity present in the raw water (Herselman, Unpublished). In general, most WTRs may be described as particulate or gelatinous substances composed of aluminium and iron hydroxides, carbonates of calcium and magnesium, inorganic particles such as clay or sand, coloured colloids, microorganisms and other organic and inorganic matter removed from the water being treated (Albrecht, 1972).

1.2.2 Physical Properties

Water treatment residues contain two primary phases, namely a solid phase (flocs) and a liquid phase (bulk water) (Babatunde and Zhao, 2007). Prior to disposal, residues are dewatered to maximise water recovery and to facilitate handling (Hughes *et al.*, 2005). The dewatered or thickened by-product (typically 28 to 30% solids) is comprised of desiccated flocs with a high surface area and extensive internal network of pores and channels (Makris *et al.*, 2005). The elevated surface area ($28 \text{ m}^2 \text{ g}^{-1}$) of an Fe-based WTR used in a study by Makris *et al.* (2004a) was attributed to small particle size and a high percentage of micropores. The majority of WTR particles were found to be in the 0.1 to 1 μm range while the volume distribution showed that the greatest volume of WTR particles was found in the range of 100 to 2000 μm (Figure 1.1). Residues typically have bulk densities between 0.56 and 1.3 g cm^{-3} , lower than the typical range for soil (1.0 to 1.55 g cm^{-3}) (Dayton and Basta, 2001) and an ‘earthy’ smell, though this is influenced by the quality of the raw water source. Table 1.1 lists the physical properties of five South African WTRs used in the study by Titshall and Hughes (2005). Particle density of the dry WTRs ranged from 2.02 to 2.43 g cm^{-3} while plant available water was generally low and ranged from 8.66 to 198 g kg^{-1} .

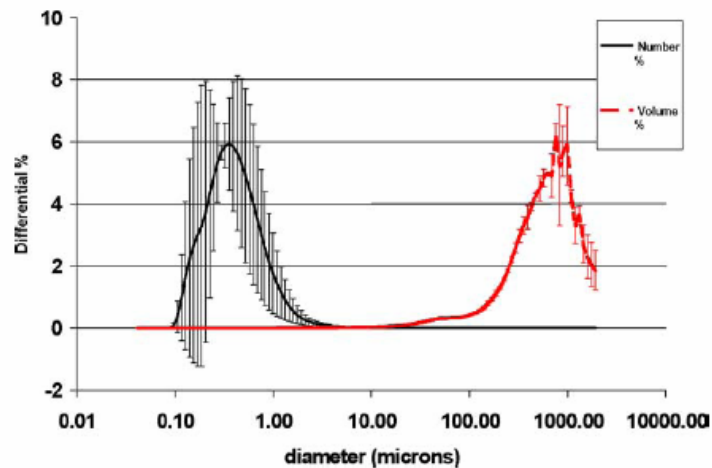


Figure 1.1 The semi-log normalized particle size distribution of an Fe-based WTR (Makris *et al.* 2004a).

Table 1.1 Some physical properties of five South African water treatment residues (Titshall and Hughes, 2005)

Property		Rand ^a	Midvaal ^b	Amatola ^c	Faure 2 ^d	Midmar ^c	Midmar ^c
		air dry					fresh
Particle size distribution (% by mass)	Sand (0.05-2 mm)	1.20	37.5	67.5	14.4	91.6	6
	Coarse silt (0.02-0.05 mm)	1.60	2.00	1.10	5.70	2.40	4
	Fine Silt (0.002-0.02 mm)	34.3	31.4	2.10	61.2	2.50	6
	Clay (<0.002 mm)	62.9	29.1	29.3	18.7	3.50	84
Particle density (g cm ⁻³)		2.43	2.09	2.02	nd	2.23	-
Plant available water (g kg ⁻¹)		18.2	40.5	8.66	198	53.8	-

^a Lime softening residue with CaO, FeCl₃, long chain polymers and activated silica.

^b Alum residue with FeCl₃, lime and long chain polymers. ^c Lime and long chain polymer residue.

^d Ferric residue with lime and long chain polymers. **nd** not determined.

In a study on fourteen alum and three polymer based WTRs from Oklahoma, Dayton and Basta (2001) found that while water holding capacities were marked (up to 360 g kg⁻¹), plant available water in some WTRs were sufficiently low to limit the use of WTR as a soil substitute. While WTRs are generally expected to have high clay and silt contents, this property is only seen if complete dispersion is achieved (Hughes *et al.*, 2007). Titshall and Hughes (2005), in demonstrating the effects of air-drying on the particle size distribution of a WTR, found clay content to be markedly

higher in a fresh, wet sample (Table 1.1). This particular residue was shown to spontaneously ‘crumble’ under alternate wetting and drying (‘self-mulching’ behaviour). The coagulation of fine particles into larger stable aggregates may, however, cause some residues to exhibit a coarse texture (Hughes *et al.*, 2005). Residues with pozzolanic (self-cementing) properties have been utilised as building and construction materials (Dunster *et al.*, 2007).

1.2.3 Chemical Properties

The chemical composition of WTRs tends to be water treatment plant specific due to the utilisation of different treatment processes and variability in raw water quality. Residues may, as noted previously, be grouped into two general categories (coagulant or softening) based on the predominant treatment additive. Coagulant residues, often termed alum or ferric residues, tend to be comprised primarily of Fe and Al while Ca and Mg make up a significant fraction of softening or lime residues (Table 1.2). In most instances, the pH of WTRs range between 5.1 and 8.0, and is dependent on the amount of lime added during the coagulation process (Ahmed *et al.*, 1997). Alum residues are often acidic due to the strong tendency of Al to hydrolyse in water (Yang *et al.*, 2006). Many WTRs, including coagulant residues, have high calcium carbonate equivalence values (> 30 %) and numerous studies (e.g. Elliott and Singer, 1988; Geertsema *et al.*, 1994) have documented the use of these residues as effective liming agents for agricultural soils. Electrical conductivity values of WTRs tend to be below 4 dS m⁻¹, a value associated with reduced plant growth due to salinity (Dayton and Basta, 2001; Titshall and Hughes, 2005). The organic carbon contents of WTRs are frequently higher than those found in typical soils due to the inclusion of activated charcoal or organic polymers during the water treatment process (Dayton and Basta, 2001). Fulvic, humic and humathomelanolic acids, which are the decomposition products of organic matter, make up a major component of the natural organic material found in WTRs (Babatunde and Zhao, 2007).

Some water treatment residues have been found to have high cation exchange capacities (CECs), a property which suggests that these materials have the ability to supply and retain cationic nutrients for plant growth. The CECs of 17 WTRs used in a study by Dayton and Basta (2001) ranged from 13.6 to 56.5 cmol_c kg⁻¹ which is greater than the typical range reported for soil (3.5 to 35.6 cmol_c kg⁻¹; Brady and Weil, 1996). High CECs have been attributed primarily to the amorphous Al and Fe fraction (Elliott *et al.*, 1990a) which usually constitute a large fraction of the total Al and Fe

Table 1.2 Chemical characteristics of coagulant (alum and ferric) and softening (lime) water treatment residues (mean values $\pm$ SD) (Babatunde and Zhao, 2007)

Parameter	Unit	Alum Residue	Ferric Residue	Lime Residue
Al	% dry weight	29.7 $\pm$ 13.3	10.0 $\pm$ 4.8	0.5 $\pm$ 0.8
Fe	% dry weight	10.2 $\pm$ 12	26.0 $\pm$ 15.5	3.3 $\pm$ 5.8
Ca	% dry weight	2.9 $\pm$ 1.7	8.3 $\pm$ 9.5	33.1 $\pm$ 21.1
Mg	% dry weight	0.89 $\pm$ 0.8	1.6	2.2 $\pm$ 1.0
SiO ₂	% dry weight	33.4 $\pm$ 26.2	nd	54.6
pH	-	7.0 $\pm$ 1.4	8.0 $\pm$ 1.6	8.9 $\pm$ 1.8
BOD ₅ ^a	mg L ⁻¹	45 (2-104)	nd	nd
P	% dry weight	0.35	0.36	0.02
Zn	mg kg ⁻¹	33.9 $\pm$ 28.0	18.7 $\pm$ 16	2.5 $\pm$ 0.7
Pb	mg kg ⁻¹	44.1 $\pm$ 38.4	19.3 $\pm$ 25.3	1.9 $\pm$ 1.1
Cd	mg kg ⁻¹	0.50	0.48 $\pm$ 0.26	0.44 $\pm$ 0.02
Ni	mg kg ⁻¹	44.3 $\pm$ 38.4	42.9 $\pm$ 39.2	0.98 $\pm$ 0.52
Cu	mg kg ⁻¹	33.7 $\pm$ 32.5	18.7 $\pm$ 25.8	3.6 $\pm$ 3.1
Cr	mg kg ⁻¹	25.0 $\pm$ 20.1	25.7 $\pm$ 21.6	1.3 $\pm$ 0.02
Co	mg kg ⁻¹	1.06	1.6 $\pm$ 1.1	0.67 $\pm$ 0.05

^a Biological oxygen demand. **nd** Not determined.

(often greater than 90 %). This non-crystalline component has a major influence on the chemical reactivity of WTRs due to its large surface area and affinity for both cationic (heavy metals) and anionic (phosphate) species (Bayley *et al.*, 2008). With respect to P sorption processes, it has been well documented that the retention of P by WTRs and soils is directly proportional to oxalate extractable (or amorphous) Al and Fe (Dayton, 1995; Haustein *et al.*, 2000; Yang *et al.*, 2006). Given that amorphous Al and Fe oxides are ubiquitous among WTRs, it is expected that these materials may have marked P retention capacities.

From a land application perspective, chemical properties such as nutrient and heavy metal contents are of particular interest. As with many other properties, nutrient content is highly variable, being dependent, to a large extent, on the quality of the raw water. In general, total N content is greater than those found in typical soils (Table 1.3) due primarily to organic constituents such as algae, detritus and organic polyelectrolytes (e.g. polyamides or polyacrylamides) (Elliott *et al.*, 1990a). Concern has been raised regarding the potential for nitrate induced groundwater contamination

(Dayton and Basta, 2001), although data from Hughes *et al.* (2005) suggests that leaching of N in its various forms is not a problem. Total P content tends to be greater than in typical soils (Table 1.3), although plant available fractions may be substantially lower due to strong adsorption to amorphous Al and Fe oxides. Dayton and Basta (2001) noted that of 17 WTRs they investigated, Mechlich III extractable P was above adequate soil levels for only one residue. Extractable Ca and Mg concentrations were, on the other hand, within and often greater than adequate soil values.

Table 1.3 Typical concentrations of selected macronutrients and heavy metals in WTRs, agronomic soils and digested sewage sludge (Elliott *et al.*, 1990a)

Parameter	WTR ^a	Soils	Digested Sewage Sludge
Total N (%)	0.6	0.5	4.0
Total P (%)	0.2	0.1	2.5
Total Organic Carbon (%)	3.0	3.0	40
Cd (ppm)	1.5	0.4	15
Cu (ppm)	134	12	800
Ni (ppm)	55	25	80
Pb (ppm)	88	15	500
Zn (ppm)	3.8	40	1700

^a Average values calculated from 71 samples taken at 7 treatment plants; 4 plants used ferric coagulants and 3 used alum.

Most studies investigating the potential toxicity of WTRs suggest that these residues should not present metal toxicity problems when disposed of to land. Results from a toxicity leaching characteristic procedure by Hughes *et al.* (2005), showed that, with the exception of Mn, concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn in six South African WTRs were below levels of concern and often below detection limits. Elevated concentrations of heavy metals, particularly Ni, tend to be found in ferric based residues, this due to the utilisation of FeCl₃ produced from steel industry waste pickle liquor (Elliott *et al.*, 1990a; Babatunde and Zhao, 2007). Elliott *et al.* (1990b) suggested that heavy metals in WTRs, when present, were likely to remain bound in forms not readily released into solution due to strong adsorption and co-precipitation with amorphous Al and Fe hydroxides. Furthermore, as noted by Elliott *et al.* (1990a), where metal concentrations were high, these were generally only 10 to 35 % of their corresponding values in sewage sludges which are routinely applied to land (Table 1.3).

1.3 Phosphate Sorption Processes

1.3.1 Phosphorus Sorption: An Introduction

Before focussing on the specific nature of phosphorus-WTR interactions, it is of benefit to briefly review measures used to quantify sorption processes. Adsorption has been defined as the net accumulation of chemical species at the interface between a solid phase and an aqueous solution phase (Sposito, 1989). It is considered a two-dimensional process, unlike precipitation which results in the formation of three-dimensional molecular structures. The term *sorption* is often preferred when the exact mechanism of retention of a sorbate by a sorbent is unknown (Sims and Pierzynski, 2005). In this case, sorption is a general term involving the chemical processes of adsorption, surface precipitation and polymerization. In this review, the terms ‘sorption’ and ‘adsorption’ are used synonymously to refer to the net retention of the sorbate (P) by the sorbent (WTR). In the context of soil chemical processes, sorption phenomena are of fundamental importance as they determine the quantity of plant nutrients, metals, pesticides and other organic chemicals that are retained on colloid surfaces. It is, therefore, one of the primary processes affecting the transport of nutrients and contaminants in soils (Sparks, 1995). Nonmechanistic and mechanistic techniques, which are two methods used to provide a quantitative measure of substance retention by sorbents, are reviewed in Section 1.4.

The sorption of P by WTRs is a complex process influenced by numerous factors ranging from residue composition to environmental conditions of temperature and pressure. In general, the process is speculated to be biphasic in nature, characterized by an initially fast sorption step followed by a more sustained absorption phase (Makris and Harris, 2006). According to Makris *et al.* (2004a), this initial sorption phase is explained by simple Coulombic interactions between the adsorbent and adsorbate and involves highly accessible surfaces such as particle exteriors and macropores. Ligand exchange (Section 1.3.2) is suspected to be the main adsorption mechanism. The slow reaction between P and metals with metal hydroxides proceeds for days or months and has been attributed to surface precipitation reactions (Section 1.3.3) or intraparticle diffusion into micropores (Makris *et al.*, 2004b; Makris and Harris, 2006) (Section 1.3.4). Phosphorus which is loosely held to WTR surfaces through Coulombic interactions is considered plant available or labile. Conversely, P which is sorbed through bidentate ligand exchange, precipitation and intraparticle diffusion is unavailable for plant uptake and considered to be ‘fixed’.

1.3.2 Adsorption

As previously noted, adsorption is a surface process which results in the retention of a dissolved substance (an adsorbate) at the interface of a solid (the adsorbent) and the solution phase (Essington, 2004). The adsorption of P to WTRs is suspected to occur through both physical (Van der Waals forces of attraction and outer sphere complexes) and chemical processes (inner sphere ligand exchange and H-bonding) (Sims and Pierzynski, 2005). Ligand exchange, where phosphate exchanges with H_2O and OH^- on the surfaces and edges of hydrous iron and aluminium oxides and carbonates (Figure 1.2), has been viewed as major mechanism of adsorption. Bonds may be monodentate or bidentate, with P adsorbed by monodentate bonds considered to be more labile than with bidentate bonds (Pierzynski *et al.*, 2005). According to Yang *et al.* (2006) evidence for this process is seen as an increase in solution pH with phosphate addition (Figure 1.3). In this case, hydroxyl release is indicative of a ligand exchange reaction between phosphate in solution and OH^- on the alum sludge surface.

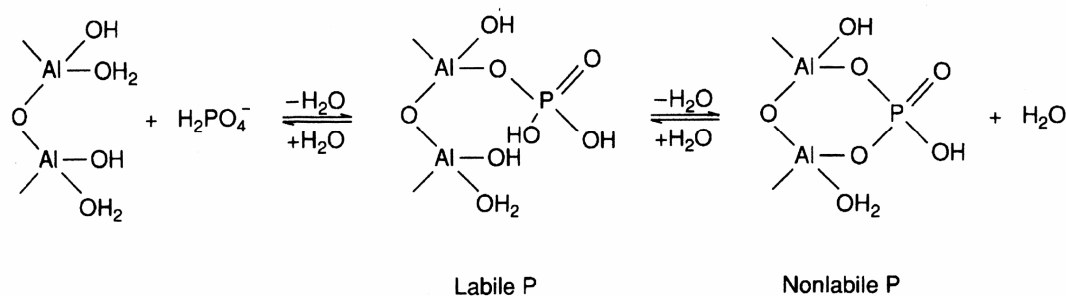


Figure 1.2 Phosphorus sorption reactions with an Al oxide, illustrating mechanisms that result in labile (centre) and non labile (right) P (Sims and Pierzynski, 2005).

Butkus *et al.* (1998) hypothesised that organic polymers, in addition to Fe and Al oxides, were responsible for a significant fraction of the P adsorbed to a ferric WTR. Models predicted that phosphate associated with quaternary polyamine constituted up to 40 % of the phosphate bound by the WTR at high P loadings. Adsorption was found to occur primarily through electrostatic interactions although ligand exchange reactions between phosphate and hydroxyl and amine functional groups were suspected to be operative. These reactions are summarised in Figure 1.4 which provides a useful overview of the major P adsorption reactions and equilibria occurring at the WTR – solution interface.

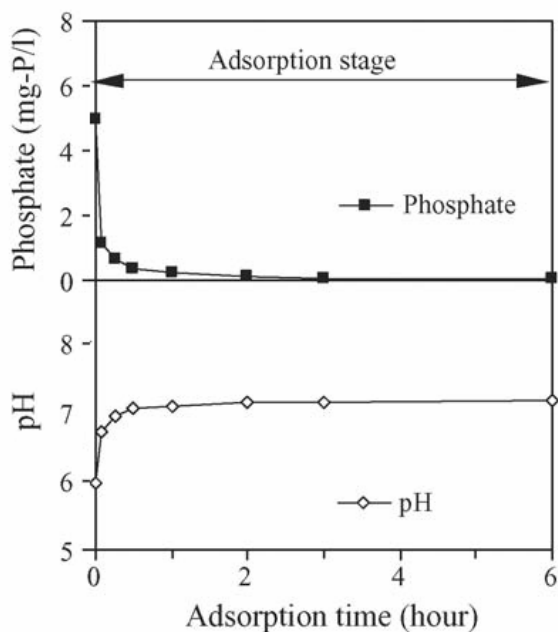


Figure 1.3 Variation of residual phosphate concentration and pH with time for an alum based water treatment residue after the application of phosphate at 5 mg L^{-1} (Yang *et al.*, 2006).

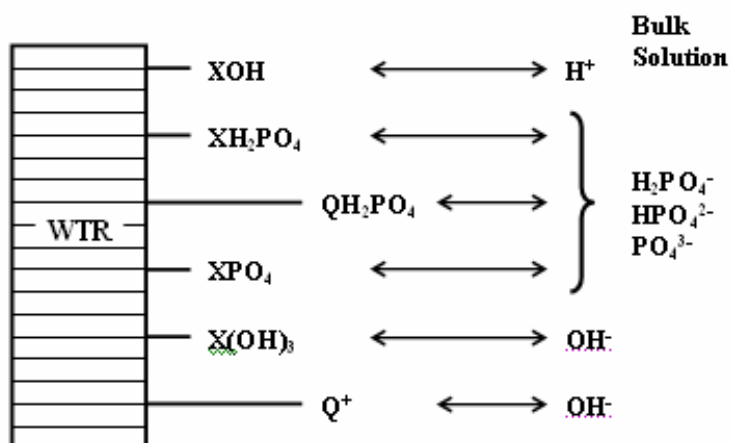


Figure 1.4 Hypothesised WTR surface reactions. X represents Fe, Al, Ca or any other hydrous oxide while Q represents an organic polymer (adapted from Butkus *et al.*, 1998).

Boisvert *et al.* (1997) concluded that ligand exchange (Equation 1) in addition to charge neutralisation (Equation 2) and proton transfer reactions (Equation 3), were responsible for phosphate adsorption on hydrolysed alum. Variations in OH/PO₄ ratios and zeta potential, that is the surface charge of the adsorbent, were used as evidence for these processes (Figure 1.5). A decline in OH/PO₄ ratio suggested the release of H⁺ (Equation 3) while a net increase confirmed a ligand exchange process (Equation 1).

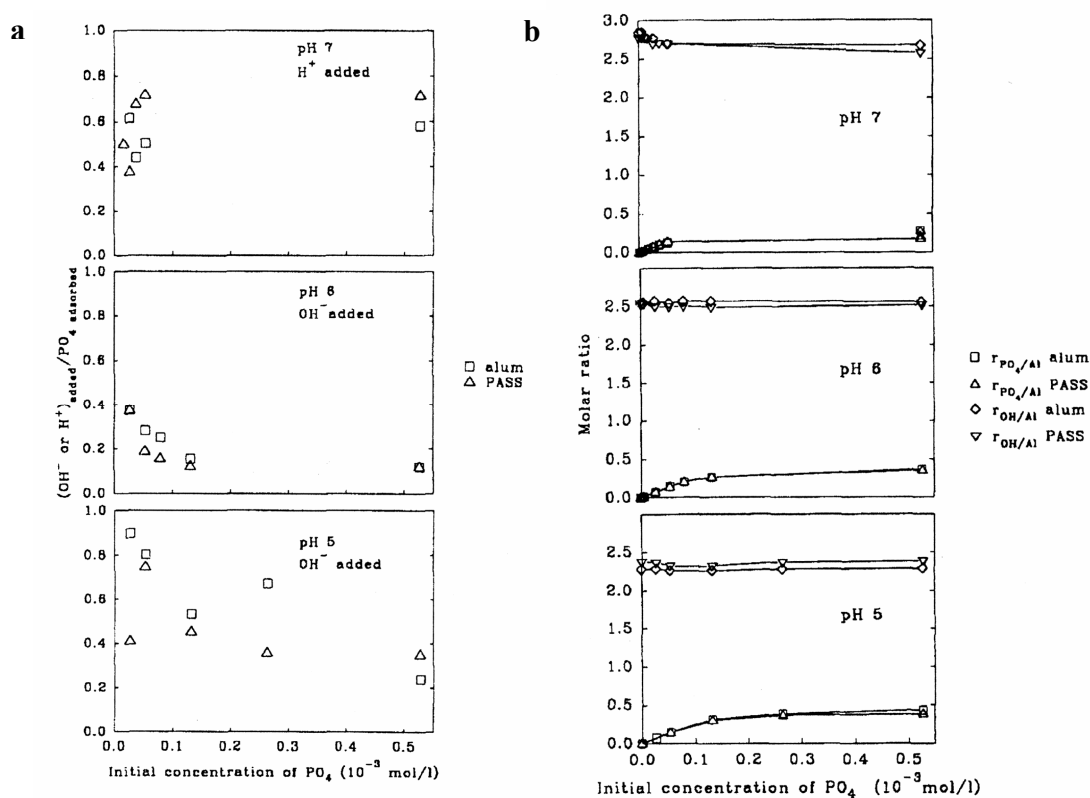
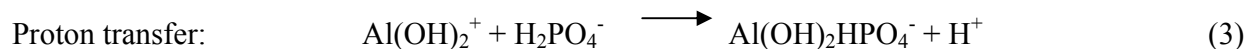
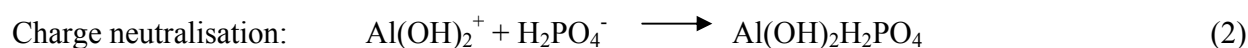
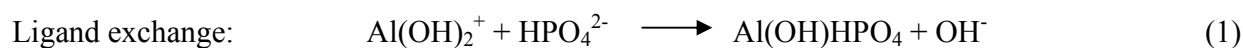


Figure 1.5 Variation of (a) OH/PO₄ ratio and (b) zeta potential with phosphate concentration for aluminium sulphate (alum) and poly-aluminium-silicate-sulphate (PASS) (Boisvert *et al.*, 1997).

With respect to zeta potential variations, a value of zero suggested complete charge neutralisation (Equation 2). Values well below zero, as seen at a pH of 7, were seen as confirmatory evidence of a ligand exchange reaction. Ligand exchange with HPO₄²⁻ ion was suspected to be favoured because

of the high affinity of the divalent ion for the $\text{Al}(\text{OH})_3$ floc at higher pH values. The exact binding or exchange reaction was, therefore, found to be dependent on pH with charge neutralisation and proton transfer dominating at a pH of between 5 and 6 (H_2PO_4^- the dominant P species) and ligand exchange dominating at a pH of 7 (HPO_4^{2-} the dominant species). It should be noted that the P-sorption mechanisms demonstrated in this study are representative of ‘ideal circumstances’ due to the utilisation of reagent grade adsorbents and pH control. The extent to which individual mechanisms are actually operative is likely to vary greatly, being dependent on the chemical composition of the WTR. The heterogeneity of WTR characteristics means that no single mechanism is likely to dominate.

1.3.3 Precipitation

Two general processes may result in the precipitation of phosphorus solid phases. Firstly, adsorption can proceed to precipitation of a P-rich solid phase if there is some degree of three-dimensional long-range atomic ordering. Secondly, P solid phases may precipitate out of solution where solubility product constants are exceeded (Pierzynski *et al.*, 2005). Both processes are associated with the fixation or permanent immobilisation of P. Given the ubiquity of soluble forms of Ca, Mg, Fe and Al in WTRs, one would expect these processes, particularly those associated with mineral equilibria, to play a major role in the sorption of P by WTRs.

Yang *et al.* (2006) demonstrated a chemical reaction between phosphate and dissolved aluminium from an alum WTR, although the extent of precipitation was found to be minimal in comparison to adsorption processes. In this case, the stability of the alum floc restricted Al dissolution thereby limiting precipitation. Dayton (1995) attempted to determine the chemical processes and components responsible for P sorption to 18 WTRs from Oklahoma. MINTEQA2 simulations showed positive saturation indices with respect to monetite (CaHPO_4) and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) for 0, 4, 10 and 14 of the 18 WTRs when equilibrated with 4, 8, 16 or 32 mg L^{-1} P solutions, respectively. While these results indicated that precipitation with Ca was favoured at higher P concentrations, batch equilibrium data showed that dissolved P decreased but dissolved Ca did not decrease. Dayton (1995) concluded that P adsorption, and not precipitation, was the dominant mechanism for P sorption during the 15 hour batch equilibration. The precipitation of calcium phosphate was, however, not ruled out and speculated to be potentially significant in the long-term.

In a study by Ippolito *et al.* (2003), MINTEQA2 modelling implied the formation of octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 2.5\text{H}_2\text{O}$) after shaking for 211 days with 300 mg P L^{-1} . While these results supported the hypothesis that long-term P chemical phase changes were associated with the Ca fraction of the WTR, electron microprobe–wavelength dispersive spectroscopy (EMPA-WDS) results suggested that this was not the case. These results showed no visible association between Ca and P but a close association between P and the Al fraction of the WTR. Based on the EMPA-WDS data, Ippolito *et al.* (2003) rejected the earlier hypothesis regarding P chemical phase changes and concluded that P was retained predominantly through chemisorption mechanisms. With time, P was found to adsorb as an inner-sphere complex eventually forming a solid phase similar to amorphous variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$).

Dayton (1995) suggested that precipitation may be inhibited simply because competing adsorption processes reduce solution P concentrations to under-saturated levels for the formation of calcium phosphate solid phases. This explanation is highly plausible given the affinity of phosphate for amorphous Fe and Al oxides which make up a major component of most WTRs. It appears, therefore, that the formation of P solid phases due to solubility products being exceeded is a negligible process unless P concentrations are sufficiently high to overcome competing adsorption reactions. In the case of alum and ferric residues, solution precipitation processes may simply be limited by the dissolution stability of the amorphous Fe and Al component (Yang *et al.*, 2006). Conversely, precipitation due to atomic ordering is of greater consequence as suggested by Ippolito *et al.* (2003). This process, which gradually occurs after the initial adsorption step, is dependent on time and relatively independent of the quantity of P adsorbed (Makris and Harris, 2006).

1.3.4 Absorption

Until recently, many studies involving the sorption of P by WTRs have involved short-term batch equilibration experiments. Knowledge regarding the mechanistic nature of P absorption processes after the initial ‘fast’ adsorption phase is therefore lacking. Most studies (e.g. Dayton, 1995; Ippolito *et al.*, 2003) have assumed that the fixation of P by WTRs is due to strong chemisorption and precipitation processes. Recently, however, a series of studies by Makris *et al.* (2004a, 2004b, and 2005) and Makris and Harris (2006) have shown that the fixation or absorption of P is due largely to the intraparticle diffusion of P into WTR micropores. The EMPA-WDS data from the study by

Makris *et al.* (2004b) showed that P moves in a three dimensional fashion towards the interior of the WTR particles rather than accumulating at the particle surface as is expected if the dominant process was precipitation. Scanning electron microscope-energy-dispersive X-ray spectrometer (SEM-EDS) data also showed no evidence of surficial metal-P phases. In this case, P was found to be evenly distributed within particles, thereby supporting an intraparticle diffusion mechanism.

Intraparticle P diffusion has been used to explain P sorption kinetics and the observation that the sorption of P by WTRs is a continual process. Makris *et al.*, (2004a) noted that the slow reaction component was indicative of a nonequilibrium reaction characterised by diffusional limitations. These limitations were attributed primarily to the large quantity of micropores present in the WTR (Figure 1.1). Apparently micropores exert a controlling influence of P-sorption processes due to their restriction on the diffusion of P molecules in and out of internal sorption sites. Intraparticle P diffusion was, therefore, suggested as the rate limiting mechanism responsible for P-sorption by WTRs. This movement into and the subsequent retention of P by WTR micropores has important implications for P desorption (Section 1.5).

1.3.5 Interactions with Organic Matter

As a common constituent of WTRs, organic matter may have a significant influence on P sorption processes. Most of this organic matter is associated with natural sources entrained in the raw water although the addition of organic coagulants may increase synthetic fractions (Makris *et al.*, 2005). There are two major views on the effects of fulvic, humic and humathomelanolic acids on P sorption to Fe and Al oxides. Phosphorus sorption capacity has, in some studies, been found to be inhibited by decomposing organic matter (Sibanda and Young, 1986; Bhatti *et al.*, 1998; Reddy *et al.*, 2001). This has been attributed to competition for P adsorption sites by organic ligands in conjunction with the dissolution of solid phases by organic acids with high Al and Fe complex constants (Bhatti *et al.*, 1998). However other studies have found P adsorption capacity to be relatively independent of the presence of organic ligands (Perrott, 1978). The affinity of phosphate for metal oxides is often stronger than the attraction between the organic acid and the mineral surface (Borggaard *et al.*, 2005). Li *et al.* (2007) noted that organic matter may actually, through complexation, inhibit amorphous Al and Fe oxides from crystallising thereby increasing P sorption capacity. Guppy *et al.*

(2005) suggested that, when present, elevated sorption capacity could be attributed to P retention by low molecular weight organic acids.

The effects of organic matter on P sorption by WTRs have been related by Makris *et al.* (2004a, 2005 and 2006) to intraparticle P diffusion. Organic carbon distribution and concentration play an important role in determining the extent of P diffusion into the interior of particles. In the study by Makris *et al.* (2005), organic carbon was found to reduce P sorption per unit pore volume or surface area by inhibiting P diffusion towards the interior of particles. Organic components, varying in size and nature, were thought to regulate the diffusion of water and phosphate molecules by becoming trapped in WTR pore networks. In this regard, organic carbon was hypothesised to be a rate-limiting factor for P sorption (Makris *et al.*, 2004a).

1.4 Methods Used to Quantify Sorption Processes

1.4.1 Nonmechanistic Techniques

Nonmechanistic techniques are based on the determination of the mass distribution of a substance between the solid and solution phases at equilibrium (Essington, 2004). This is most commonly achieved by relating the equilibrium surface excess (S) (amount of a compound adsorbed) to the equilibrium solution concentration (c) of the compound. The variation of S with respect to c may then be mathematically described to elucidate the adsorption behaviour of a particular substance (Essington, 2004).

At fixed temperature, pressure and solution chemistry these relationships have been termed *sorption isotherms*. However, as Barrow (1978) highlights, factors other than temperature and concentration may affect S/c relationship in a soil system and the term *isotherm* implies a degree of control which does not exist. Essentially, the use of isotherm equations involves a curve fitting procedure implying isotherm parameters are valid only for the chemical conditions under which the experiment was conducted (Goldberg, 2005). It is also important to note that conformity to a particular empirical equation does not necessarily mean that the model from which it was generated was appropriate (Barrow, 1978). Because sorption isotherms are only descriptions of macroscopic data and do not definitively prove a reaction mechanism (Sparks, 1995), independent experimental evidence of an adsorption process is required before any chemical meaning can be assigned to isotherm equation

parameters (Goldberg, 2005). The four common equilibrium-based adsorption models reviewed here include the Langmuir, Freundlich, Temkin and the linear or distribution coefficient equations.

1.4.1.1 Linear Equation

The simplest and most widely used adsorption isotherm is that given by a linear relationship between S and c :

$$S = K_d \cdot c + a$$

where S is the amount of adsorbate (e.g. phosphate) adsorbed per unit of adsorbent (e.g. WTR), c is the adsorbate concentration in solution (or residual P concentration) and a is the y-intercept. In this case, S is related to c through the distribution coefficient K_d which provides a measure of adsorbate retention (Travis and Etnier, 1981). Conformity of a set of sorption data to this model suggests that S is independent of sorption site saturation. Because of the linear assumption, this equation usually describes ion adsorption data across a restricted solution ion concentration range (Goldberg, 2005).

1.4.1.2 Langmuir Equation

The Langmuir adsorption isotherm was initially developed to describe the adsorption of gases onto clean surfaces and may be written as:

$$S = K \cdot c \cdot x_m / (1 + K \cdot c)$$

where S and c are as previously described, x_m is the maximum adsorption per unit mass and K is an affinity parameter related to the bonding energy of the adsorbing surface. Determination of the parameters K and x_m is commonly achieved by plotting c/S against c . The model is based on three assumptions (Atkins and de Paula, 2002):

1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform.

3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. This assumption supposes that there are no interactions between adsorbed molecules.

A key assumption of the Langmuir monolayer theory is that the free energy of adsorption (described by the parameter K) remains constant and is independent of the number of occupied adsorption sites (Travis and Etnier, 1981). Because these assumptions do not hold true for heterogeneous materials such as soils and WTRs, the Langmuir equation is seldom applicable from a mechanistic perspective (Dayton, 1995). The model has, nevertheless, been used extensively to describe sorption data and is particularly useful when quantifying upper limits of adsorption.

1.4.1.3 Freundlich Equation

The Freundlich equation, which is the oldest of the nonlinear sorption isotherms, was first used to describe gas phase and solute adsorption (Sparks, 1995). Unlike the Langmuir isotherm, the enthalpy of adsorption is assumed to be dependent on the occupation of adsorption sites. In this case, the heat of adsorption (distribution coefficient) is a logarithmic function of surface coverage. The isotherm is described as:

$$S = K \cdot c^a$$

where S and c are as previously described, K is the distribution coefficient and a is a correction factor relating to the heterogeneity of adsorption sites, where the smaller a is, the greater the expected heterogeneity (Goldberg, 2005). Although this particular isotherm does not invoke any physical model, adherence to the Freundlich isotherm corresponds to a model of adsorption in which the affinity term (K) decreases exponentially as the amount of adsorption increases (Barrow, 1978). One limitation of the Freundlich isotherm is that, like the linear isotherm model, it does not imply a maximum quantity of adsorption. The equation may be linearized by plotting $\log S$ against $\log c$.

1.4.1.4 Temkin Equation

The model from which the Temkin equation is derived is one in which the affinity term (K_1) decreases linearly as the amount of adsorption increases (Barrow, 1978). In contrast to the

Freundlich equation, the Temkin equation assumes that the heat of adsorption is a linear function of surface coverage (Travis and Etnier, 1981). In its simplest form, the equation may be written as:

$$S = K_1 \cdot \log (K_2 \cdot c)$$

where S and c are as previously described K_1 is the affinity parameter and K_2 is a coefficient. In this case, a decreasing affinity term suggests that the energetically most favourable sites are occupied first (Atkins and de Paula, 2002). The parameters K_1 and K_2 may be determined by plotting S against $\log c$.

1.4.2 Mechanistic techniques

Mechanistic techniques are based on relating the equilibrium surface excess to a solution property other than substance concentration. This may, for example, involve an evaluation of adsorption as a function of solution pH (Essington, 2004). As the term implies, mechanistic techniques give quantitative insight into potential adsorption mechanisms and often involve the use of chemical surface complexation models. Such models may, for example, consider surface charge arising from protonation-dissociation and ion surface complexation reactions. Many of these models are descriptions of adsorption processes whose molecular features can be given thermodynamic significance (Goldberg, 2005).

Despite their limitations, nonmechanistic methods have been utilised more extensively than mechanistic techniques. This has been attributed in part to their simplicity as well as the ease of estimation of their adjustable parameters (Goldberg, 2005). The description of adsorption data with empirical isotherm equations has the added benefit of allowing the properties of an adsorbent to be summarized using a few numbers rather than having to refer to a curve (Barrow, 1978).

1.5 Phosphate desorption processes

Desorption has been defined as the release of a sorbate from a sorbent into the solution phase, without reference to any specific mechanism (Sims and Pierzynski, 2005). Desorption may, therefore, encompass both exchange and dissolution reactions. In the context of WTR-P relations,

desorption processes are of fundamental significance since they govern P adsorption by plants, leaching and the transportation of P in runoff water. Unlike sorption processes, however, which have been examined extensively, very few studies have focussed on the release of P from WTRs and the factors influencing P availability in agronomic and environmental contexts. This could be due, in part, to the fact that quantifying readily extractable pools of P is hindered by strong chemisorption and precipitation processes. These processes result in a hysteretic effect whereby desorption follows a completely different pathway or set of mechanisms to the adsorption processes. As with adsorption, desorption processes are further complicated by residue heterogeneity and environmental variability.

The desorption of P from WTRs may be described by two distinct mechanisms, namely disequilibria desorption and ligand desorption. Disequilibria desorption is based on the common observation that reducing the P concentration in solution promotes desorption from the solid phase (Le Chatelier's Principle) (Sato and Comerford, 2006b). Ligand desorption, on the other hand, involves the release of inorganic P in response to the action of ligands exchanging with phosphate or dissolving phosphate bearing compounds (Sato and Comerford, 2006a). These ligands, which include common organic anions such as oxalate, citrate and bicarbonate (common constituents of root exudates), have the ability to extract a greater quantity of inorganic P than simple disequilibrium processes. Ligand desorption processes could, therefore, be potentially significant with respect to the land application of WTRs and plant P deficiencies. Of particular interest is the observation that under field conditions, plants growing on WTR amended soils exhibit no signs of P deficiency. Hughes *et al.* (2005), for example, found that differences in extractable P between the soils on control plots compared to WTR-treated plots were small while perennial ryegrass growing on mulched plots (pure WTR) showed no indication of P deficiency. The growth of these plants in a layer of WTR suggests that the P present in the residue was accessible for the duration of trial through one or both of the aforementioned processes. The relevance of these processes with respect to WTRs is thus reviewed.

1.5.1 Disequilibria Desorption

In disequilibria desorption studies, P release is frequently examined by diluting a P-loaded sample with a solution of known ionic strength for a given time. In one such study involving variable

shaking times, Ippolito *et al.* (2003) found that the quantity of P desorbed from an Al and Ca based WTR decreased with an increase in shaking time. Evidence for a continual sorption process, involving an initially fast adsorption phase followed by a sustained period of absorption process, was seen in the increase in solution pH with time (Figure 1.6). The desorption of P via disequilibria processes was apparently negligible given that, of the original 12 500 mg P adsorbed, between 4.7 and 17.3 mg P was released back into solution. Ippolito *et al.* (2003) concluded, therefore, that the inhibition of P desorption through strong chemisorption (Section 1.3.2) made WTRs poor suppliers of P.

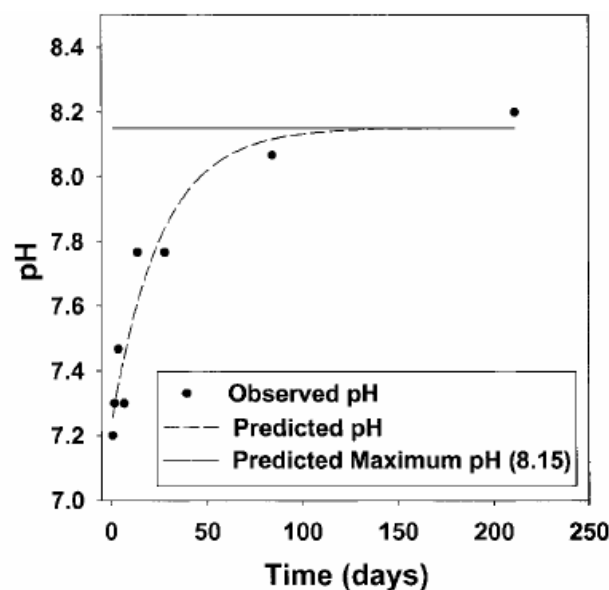


Figure 1.6 Variation in solution pH with shaking time for a P-loaded WTR (Ippolito *et al.*, 2003).

In contrast, Butkus *et al.* (1998) suggested that the pre-treatment of WTR with sufficient P could convert WTRs from P consumers to P suppliers. The binding of P to organic polyelectrolytes following the saturation of hydrous Fe and Al oxide sites, was given as a possible reason for positive plant response to P amended WTR. The models used in the study by Butkus *et al.* (1998) were, however, based on PO_4 pre-treatment values of between 1.25 and 6.0 mol kg^{-1} WTR (equivalent to between 119 and 570 g PO_4 kg^{-1} WTR). The addition of P in such high quantities is uneconomical given the cost of inorganic fertiliser. So while pre-treatment may increase disequilibria desorption pools of P, the quantities of P required for effective implementation appear unfeasible. Furthermore,

the prevalence of continual P-sorption processes (Section 1.3.4.) suggests that pre-treatment effectiveness will decline with time.

1.5.2 Ligand Desorption

The observation that plants, through the release of root exudates, are able to increase P uptake (Parfitt, 1979; Johnson and Loeppert, 2006) is of particular interest with respect to P availability in WTR amended soils. Phosphorus mobilisation by organic ligands has been attributed to the enhanced dissolution of P minerals caused by acidification and complexation of cations such as Ca, Fe and Al, and to the competitive adsorption of phosphate and organic ligands on metal hydrous oxides (Geelhoed *et al.*, 1999). In a study on the influence of oxalate on P desorption from a spodic horizon, Bhatti *et al.* (1998) concluded that organic ligands could significantly increase P availability in P deficient soils. The operation of ligand desorption mechanisms could, therefore, be a plausible explanation for the absence of plant P deficiencies in WTR amended soils. This form of desorption is of particular interest given that disequilibria desorption pools are seemingly restricted by P immobilisation processes (chemisorption and precipitation).

The only current study that investigated the effect of an organic ligand on the release of P from WTRs is that of Makris *et al.* (2005). Seven WTRs (previously treated with P) were shaken with a 5 mM oxalate solution for 1, 10, 20, 40 and 80 days to test the ability of a common soil organic ligand to desorb P from the WTR. As in the study by Ippolito *et al.* (2003), desorption of P from the WTRs decreased with increasing time, suggesting a continuous sorption process. They found that after 40 and 80 days, soluble P concentrations were below P detection limits (0.3 mg L^{-1}) suggesting limited desorption. With shorter contact times (between 1 and 20 days), P desorption was minimal (between 0.2 and 1.3 % and 1.3 and 8.3 % of P adsorbed for alum and ferric residues, respectively). Makris *et al.* (2005) suggested that, in addition to strong chemisorption, P release was inhibited by restricted ligand access to WTR-P sites and that significant P desorption from WTRs required particle dissolution.

The release of P through both ligand and disequilibria desorption processes is apparently hindered by intraparticle diffusion into WTR micropores (Section 1.3.4). In the case of disequilibria desorption, diffusion of water to and from adsorption sites is inhibited by narrow pores sizes and the transport of loosely held P away from WTR surfaces is subsequently restricted (Makris *et al.*,

2004a). In the case of ligand desorption, diffusion of P into micropores restricts the access of complexing ligands such as oxalate and citrate (Makris *et al.*, 2005). The sorption of P by WTRs is therefore, seemingly irreversible unless disintegration of the particles occurs (Makris *et al.*, 2004b). While this may appear to contradict field trial observations, it is important to note that the studies by Makris *et al.* (2004a, 2004b and 2005) were focussed on the long-term stability of sorbed P under the land application of WTRs to P-sensitive ecosystems. In Makris *et al.*'s (2005) study, for example, the P detection limit utilised (0.3 mg L^{-1}) was significantly higher than the value reported by Zupancic (1996) (0.05 mg L^{-1}) as being adequate for plant growth. This suggests that while the quantities of P desorbed from WTRs are not significant from an environmental perspective, sufficient P may be desorbed to sustain and even promote plant growth. Water treatment residues could, therefore, be utilised as both eutrophication preventatives and slow release P fertilizers. Further research is required to substantiate this suggestion.

1.6 Conclusions

Most, if not all, of the studies reviewed here have documented the ability of WTRs to adsorb substantial quantities of phosphate (P). These sorption capacities have been attributed to the extent or number of P-reactive sites in WTRs in conjunction with the affinity of these sites for P. It is widely accepted that amorphous Al and Fe oxides, which are a major component of many WTRs, play a notable role in P sorption processes due to their large surface area and chemical affinity for P. Calcium content, organic matter content and residue pH are also important in determining the extent to which P is retained or released. It is important to note that WTRs are chemically heterogeneous and that the chemical processes relating to P sorption and desorption tend to be residue specific.

Mechanistically, P sorption by WTRs is a biphasic process characterised by a rapid adsorption step followed by a more sustained absorption phase. Initially, P is quickly sorbed to highly accessible particle exteriors and mineral surfaces through ligand exchange, charge neutralisation and proton transfer reactions. Phosphate adsorbed during this stage is 'weakly' held and considered plant available. Over time, however, a significant fraction of adsorbed P becomes fixed (absorbed) into non-labile fractions unavailable for plant uptake. Although Makris *et al.* (2004a, 2004b, 2005) have shown that this fixation is due primarily to intraparticle P diffusion, chemisorption and precipitation

remain important and potentially significant processes. This permanent immobilisation of P is perhaps the central issue with respect to the land application of WTRs.

The majority of studies reviewed here suggest that the utilisation of WTRs, in an agricultural context, will be restricted by inducing growth inhibiting plant P deficiencies. In addition to the rapid sorption of labile P fractions, P release from WTRs is greatly inhibited by physio-chemical limitations. Studies involving field trials have, however, clearly demonstrated that P immobilisation is not a serious concern. The absence of plant P deficiencies in the field has to be attributed to one or more of the following processes:

1. plant P deficiencies are absent because WTRs have little effect on soil P chemistry (a dilution effect);
2. sorption of P onto WTRs in the field is restricted or inhibited; or
3. that plants growing in the field have the ability or mechanisms to extract sufficient P from the residues.

The lack of research into field based applications in conjunction with residue heterogeneity means that it is difficult to assess the extent to which these processes are operative. Based on the findings of Hughes *et al.* (2005), where ryegrass grew adequately in pure WTR, P had to have been accessible to plant roots. It is also worth noting that most plants only require a residual P concentration (soil solution concentration) of between 0.05 and 0.2 mg L⁻¹ for adequate growth. This suggests that seemingly insignificant desorption process may actually release sufficient P for plant growth. The magnitude of P sorption-desorption processes must, therefore, be interpreted in either an agricultural or environmental context.

CHAPTER 2

THE CHEMICAL CHARACTERISATION AND DISTRIBUTION OF PHOSPHORUS IN WATER TREATMENT RESIDUES

2.1 Introduction

The chemical properties of water treatment residues (WTRs) have been well documented with many studies confirming their benign nature (e.g. Dayton and Basta, 2001; Titshall and Hughes, 2005). Water treatment residues are, nevertheless, heterogeneous and characterisation is a prerequisite for successful land application. Of particular interest are the chemical properties relating to their high P sorption capacities. Properties such as pH, Ca, organic carbon and amorphous Al and Fe content have been shown to directly influence P sorption processes (Dayton, 1995; Boisvert *et al.*, 1997; Makris *et al.*, 2005) and are, therefore, important to quantify. Of additional interest is the inherent P content and the distribution of this P within the WTRs. Quantifying labile and non-labile P pools is essential in an agricultural context as P is often a limiting nutrient for plant growth, and from an environmental context as excess P leads to surface water eutrophication. In addition to this, an understanding of the distribution of P in WTRs is required if sorption-desorption processes are to be correctly interpreted. However, few studies have focussed on the fractionation of P in WTRs into the various components.

The aim of this study is to characterise the chemical properties of 15 South African WTRs relevant to P sorption-desorption processes. In addition, the distribution of P within the WTRs will be determined using a chemical fractionation procedure, which includes separating the inherent P in the WTRs into labile (plant available) and non-labile (chemisorbed) fractions.

2.2 Materials and Methods

2.2.1 Water Treatment Residues

Fifteen WTRs from a range of South African water treatment plants were selected for study (Table 2.1). Selected chemical properties of the WTRs, which were collected for another study to develop disposal guidelines, were previously described by Herselman (Unpublished; Appendix 2.1). All

analyses were carried out on WTRs that were air-dried, ground to pass a 2mm sieve and stored in screw-top plastic bottles.

2.2.2 Chemical Characterisation

The chemical analyses focussed on WTR properties that were relevant to sorption-desorption processes. These included pH, P content and distribution, Ca content, organic carbon content and dithionate, oxalate and pyrophosphate extractable Al and Fe. pH was measured in distilled water using a Meter Lab PHM 210 pH meter with a standard glass electrode in a WTR: solution ratio of 1:2 (10 g WTR:20 ml distilled water) after shaking for an hour on a reciprocal shaker (Dayton, 1995). Total P was calculated as the sum of the fractionated components (Section 2.2.3). Exchangeable Ca, ammonium bicarbonate (Ambic) extractable P and oxidisable organic carbon content data were obtained from Herselman (Unpublished). Three separate extractions were used to determine extractable Al and Fe. A dithionate-citrate-bicarbonate extraction (0.3 M citrate, 1 M bicarbonate, dithionate added in excess) (Mehra and Jackson, 1960) was used to determine the total quantities of free Al and Fe oxides. Extracts were analysed for Al and Fe by atomic adsorption spectroscopy (AAS) on a Varian Spectra AA-200. Oxalate extractable Al, Fe, Ca and P were determined after extraction with acid ammonium oxalate (0.175 M) at pH 3 (Loeppert and Inskeep, 1996). All residues were pre-treated with ammonium acetate to prevent the precipitation of Ca-oxalate salts. After extraction, samples were centrifuged at 3500 rpm for 10 minutes and analysed for Al, Fe, Ca and P using a Varian (720 ES) inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Phosphorus extracted during this procedure (P_{ox}) was assumed to be bound to the amorphous Al (Al_{ox}) and Fe (Fe_{ox}) component. The P-saturation index for each residue was calculated as the molar ratio of P_{ox} to the sum of Al_{ox} and Fe_{ox} (Elliot *et al.*, 2002). Organically bound Al and Fe were determined by means of a sodium pyrophosphate extraction (0.1 M) (McKeague, 1967). Extracts were analysed for Al and Fe by AAS. All extractions, with the exception of the pyrophosphate extraction (0.3 g samples) were carried out in duplicate on 0.5 g samples.

2.2.3 Phosphorus Fractionation

The distribution of inherent P in the 15 WTRs was determined using a sequential phosphorus extraction (Zhang and Mackenzie, 1997) on duplicate 0.5 g samples. This procedure identified

soluble and loosely held P (bicarbonate extraction), Al and Fe oxide surface bound P (NaOH extraction), Ca bound P (HCl extraction) and residual P (H_2SO_4 digestion) (Appendix 2.2). Aliquots of the bicarbonate and hydroxide extracts (10-15 ml) were acidified with 2 M HCl to precipitate extracted organic matter and the supernatant analysed for inorganic P (P_i). The remaining bicarbonate and hydroxide extracts were analysed for total P after a $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}_2$ digestion (Zhang and Mackenzie, 1997). The difference between total P and P_i was considered to be organically bound (P_o). This allowed soluble and loosely held P and Al and Fe oxide surface bound P to be fractionated into their respective inorganic and organic components. Plant available P_i was estimated by extracting with 1 M bicarbonate and 0.1 M NaOH. Inorganic P in all extracts and digestion solutions was determined colorimetrically by the molybdate blue method (Murphy and Riley, 1962).

2.3 Results and Discussion

2.3.1 Chemical Characterisation

The range in pH values for the 15 WTRs (4.77 to 8.37) (Table 2.1) was greater than that of 17 residues from Oklahoma (5.29 to 7.77; Dayton, 1995). In most cases, WTRs were alkaline with the exception of the Churchill, Elandsjagt and Loerie residues. Calcium contents ranged from 238 mg kg^{-1} in the acidic Churchill residue to 8 980 mg kg^{-1} in the carbonate-rich Droogdam residue. The range of these values suggests varying potential for the formation of insoluble calcium phosphates. Amorphous Al (Al_{ox}) and Fe (Fe_{ox}) ranged from 1 401 to 82 947 mg kg^{-1} for Al and 3 865 to 140 569 mg kg^{-1} for Fe (Table 2.1). Dayton (1995) measured ranges of 808 to 78 840 and 1 303 to 19 656 mg kg^{-1} for Al_{ox} and Fe_{ox} , respectively for 17 WTRs in Oklahoma. This non-crystalline component is of particular relevance with respect to P sorption due to its large surface area and chemical affinity for phosphate. The P saturation index (PSI) values show that for $\text{PSI} < 1$ there is an excess of reactive Al and Fe while $\text{PSI} > 1$ indicates that reactive components are saturated by an excess of P (Elliot *et al.*, 2002). Therefore, residues with low PSI values (e.g. Bronkhorstspuit and Faure residues) have a higher potential for P sorption than residues which have a greater quantity of inherent P (e.g. Bloemfontein and Droogdam residues) (Table 2.1). Values were, nonetheless low which suggests that all WTRs have the potential to adsorb significant quantities of P. However, Elliot *et al.* (2002) have noted that PSI values are not as reliable a measure of P-fixing ability in Ca-based WTRs due to unique P removal mechanisms. In the Droogdam residue, for example, where the PSI is elevated due to a high P content, the high P sorption potential is most

likely maintained by the high Ca content of this WTR (Section 2.3.2). Organic carbon (OC) contents, which varied between 0.50 and 11.6 % (Table 2.1), were related to the characteristics of the water treatment chemicals and raw water quality.

Table 2.1 Selected chemical characteristics of 15 South African water treatment residues

WTR	pH	Ca ^a	Dithionate ^b		Oxalate ^c		Pyrophosphate ^d		PSI	OC
		mg kg ⁻¹	Al	Fe	Al	Fe	Al	Fe		
			mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹			%
Blackheath	7.04	1613	96375	2565	44727	6240	37200	11400	0.017	9.13
Bloemfontein	7.56	3782	1171	700	2536	8980	310	840	0.139	2.07
Bronkhorstspuit	7.77	3080	78000	981	82947	75985	4070	1340	0.008	11.6
Churchill	5.92	238	19038	2978	36624	6178	24500	6400	0.006	9.93
Droogdam	7.25	8980	741	5263	2822	53419	390	7470	0.116	3.26
Elandsjagt	6.93	1080	17975	2059	33638	140569	9910	2500	0.006	7.55
Faure	7.56	5577	12800	15288	4507	10341	5880	90000	0.009	4.45
Loerie	4.77	575	7063	1186	12615	9736	14850	7530	0.018	4.74
Midmar	7.29	3860	1583	2526	6260	5442	1150	1140	0.042	3.85
Nahoon	7.82	2760	1228	1486	2953	18866	350	740	0.072	2.56
Nelspruit	7.44	2387	1139	1836	2546	21176	3470	3140	0.098	0.50
Noditgedagt	7.54	3691	936	2524	2083	3865	270	4070	0.091	1.27
Randwater	8.37	1311	1283	441	3234	21342	130	230	0.065	0.72
Vaalkop	7.25	3433	1613	2134	1401	5338	1250	7410	0.056	0.57
Voelvlei	8.02	3747	1909	7113	1980	5952	200	1250	0.013	0.91

^a Data from modified from Herselman (Unpublished).

^b Dithionate extractable. ^c Oxalate extractable. ^d Pyrophosphate extractable Al and Fe.

PSI Phosphorus Saturation Index ($PSI = [P_{ox}]/[Al_{ox}] + [Fe_{ox}]$). **OC** Organic Carbon (Herselman, Unpublished).

Dithionate extractable Al (Al_{di}) and Fe (Fe_{di}) varied considerably from 741 to 96 375 mg kg⁻¹ for Al and from 441 to 15 288 mg kg⁻¹ for Fe (Table 2.1). This extraction, which removes finely-divided, crystalline mineral phases, amorphous inorganic Al and Fe and organic-complexed components, provides a measure of total “free” Al and Fe oxide contents. Therefore, it was not expected that dithionate fractions would be, for the majority of residues, less than the poorly crystalline fractions removed with the oxalate extraction. Loeppert and Inskeep (1996) have noted that the dissolution efficiency of the dithionate reagent is strongly affected by particle size. Therefore, dithionate extraction efficiency may have been inhibited due to insufficient grinding of the samples although

the ease with which amorphous components are dissolved does suggest that particle size variation is of limited importance. Pyrophosphate extractable Al (Al_{py}) and Fe (Fe_{py}) values, which varied from 130 to 37 200 mg kg⁻¹ for Al and from 230 to 90 000 mg kg⁻¹ for Fe (Table 2.1), were generally less than oxalate and dithionate extractable fractions. Aluminium and Fe extracted in this procedure are considered organically bound and may consist of crystalline and amorphous fractions. Elevated values (e.g. Blackheath and Faure residues) may, therefore, reflect the additional dissolution of poorly ordered Al and Fe phases not associated with organic matter (Bertsch and Bloom, 1996). The observed direct relationship between oxalate and dithionate extractable fractions (Appendix 2.3) does provide support for this contention. The strong positive correlation between Al_{ox} and organic carbon content does, nevertheless, suggest that a proportion of the amorphous component is associated with organic matter. This has important implications with respect to P sorption processes given the greater reactivity of organic Al compared to mineral bound fractions (Bertsch and Bloom, 1996).

2.3.2 Phosphorus Fractionation

Total P concentrations ranged from 1 149 to 1 727 mg P kg⁻¹ (Table 2.2), which is within the typical range for WTRs (300 to 4 000 mg kg⁻¹; Dayton *et al.*, 2003). These values are markedly lower than P concentrations reported for sewage sludges (10 500 mg kg⁻¹; Wang, 1997) and within the typical range for soils (200 to 5 000 mg P kg⁻¹; Lindsay, 1979). The fractionation data (Table 2.2) suggests that most of the P is present in forms that are not readily available for plant uptake as the soluble inorganic P and the inorganic P held on mineral surfaces through weak chemical interactions only comprised a small fraction of total P (Table 2.2). With the exception of the Droogdam and Noditgedagt residues, over 98 % of fractionated P was bound as organic, calcium and residual forms.

The Ambic 1 extractable P concentration of the WTRs is generally lower than in typical South African soils (Table 2.3). The elevated Ambic 1 P concentrations of the Bloemfontein, Droogdam, Midmar and Noditgedagt WTRs may be attributed to a concentrating effect during the dewatering and coagulation water treatment processes. These high P concentrations are beneficial from an agronomic perspective and suggest that the land application of selected residues may be beneficial for P deficient soils. The high concentration of P present in the fixed fractions for all WTRs does, however, indicate that P buffer capacities are limited.

Table 2.2 Fractionation of P within 15 South African WTRs. Bold value represents the ratio of P fractionated to total P (%), while values in parentheses are the amount of P extracted for each component (mg kg⁻¹)

WTR	Total P fractionated						P _{Tot} ^b (mg kg ⁻¹)	P _{ox} ^c (mg kg ⁻¹)
	Bicarbonate		NaOH		HCl	Residual P		
	P _i ^a	P _o ^a	P _i	P _o	P _i	P _i + P _o		P _i + P _o
Blackheath	0.33 (4.63)	21.6 (303)	0.96 (13.5)	24.2 (339)	0.85 (11.9)	52.1 (730)	1403	69.9
Bloemfontein	0.91 (10.4)	27.3 (314)	0.50 (5.79)	27.4 (315)	1.91 (22.0)	41.9 (482)	1149	71.3
Bronkhorstspuit	0.36 (5.23)	18.5 (270)	0.94 (13.7)	19.1 (280)	1.67 (24.5)	59.4 (870)	1463	56.3
Churchill	0.33 (4.57)	21.3 (295)	0.35 (4.92)	19.3 (269)	0.86 (12.0)	57.8 (803)	1389	22.8
Droogdam	1.78 (30.7)	16.2 (281)	7.17 (124)	8.42 (146)	12.1 (209)	54.3 (938)	1727	30.5
Elandsjagt	0.33 (4.53)	21.4 (295)	0.60 (8.24)	22.5 (310)	0.81 (11.1)	54.3 (746)	1374	18.3
Faure	0.34 (4.51)	22.3 (297)	0.41 (5.44)	24.2 (322)	1.13 (15.0)	51.6 (686)	1329	57.2
Loerie	0.38 (4.89)	25.1 (321)	0.46 (5.86)	25.2 (323)	0.84 (10.8)	48.0 (615)	1280	25.0
Midmar	0.42 (5.90)	18.1 (256)	0.43 (6.09)	22.9 (324)	1.13 (16.0)	57.1 (808)	1416	55.9
Nahoon	0.47 (5.29)	26.6 (299)	0.46 (5.19)	26.5 (298)	1.03 (11.6)	44.9 (505)	1123	42.8
Nelspruit	0.35 (4.60)	24.4 (322)	0.36 (4.75)	23.1 (305)	2.71 (35.8)	49.1 (648)	1321	32.6
Noditgedagt	1.06 (14.5)	22.2 (304)	1.02 (14.0)	21.0 (288)	2.15 (29.5)	52.6 (721)	1371	93.8
Randwater	0.34 (5.03)	20.5 (300)	0.30 (4.40)	21.1 (310)	1.31 (19.2)	56.4 (827)	1466	31.8
Vaalkop	0.32 (4.62)	19.3 (283)	0.31 (4.47)	20.6 (301)	0.73 (10.7)	58.7 (858)	1461	19.4
Voelvlei	0.29 (4.46)	18.5 (281)	0.30 (4.50)	19.3 (294)	0.70 (10.7)	60.9 (928)	1523	26.6

^a P_i and P_o refer to inorganic and organic components respectively.

^b Total P values were obtained from the sum of the of bicarbonate, NaOH, HCl and residual P fractions.

^c Oxalate extractable P.

Table 2.3 Comparison of plant available and plant unavailable P fractions for 15 South African WTRs

WTR	Plant Available		Plant Unavailable
	Fractionation ^a	Ambic 1 P ^b mg kg ⁻¹	
Blackheath	18.1	4.39	1384
Bloemfontein	16.2	24.8	1133
Bronkhorstspuit	18.9	7.10	1444
Churchill	9.50	3.04	1379
Droogdam	154	34.9	1573
Elandsjagt	12.8	6.42	1361
Faure	9.95	4.62	1319
Loerie	10.7	14.4	1269
Midmar	12.0	23.4	1404
Nahoon	10.5	11.8	1112
Nelspruit	9.34	5.07	1311
Noditgedagt	28.5	37.0	1343
Randwater	9.45	13.1	1456
Vaalkop	9.09	1.01	1452
Voelvtlei	8.96	2.59	1514
Shortlands soil ^c		1.64	
Hutton soil ^c		3.54	
Oakleaf soil ^c		12.8	

^a Plant available P for the fractionation is the sum of the bicarbonate and NaOH inorganic P extractions.

^b Data from Herselman (Unpublished).

^c Ambic 1 P values for three South African soils (Henry and Smith, 2005).

This has been demonstrated by Dayton and Basta (2002) who found that tomatoes grown on WTRs exhibited P deficiency even when Olsen and Mehlich III extractable P values were within adequate soil levels. This suggests that WTRs are unlikely to make a positive contribution to bioavailable P pools unless unavailable P is released from the fixed fractions through exchange or dissolution mechanisms (Chapter 4). A marked amount of P in the WTRs was present in organically bound forms and though not considered plant available, mineralisation of this fraction may increase bioavailable inorganic P pools. The poor correlation between the sum of organic P fractions (extracted with bicarbonate and hydroxide) and OC ($r = -0.11$) (Appendix 2.3) could be attributed to

heterogeneity within the organic component. In the Nelspruit residue, for example, a low OC content (0.50 %) and high total P_0 fraction (47.5 %) suggests a P-rich carbon source. In contrast the Bronkhorstspuit residue has a high OC content (11.6 %) and lower total P_0 fraction (37.6 %). The elevated P_0 values for the residues, especially those with low OC contents, may be partly due to analytical deficiencies of the colorimetric P determination step. Condron *et al.* (2005) suggested that the inability of colorimetric techniques to account for complex inorganic P forms such as polyphosphate and pyrophosphate, may result in an overestimation of organic P during fractionation procedures. In addition to this, the complexation of orthophosphate to organic matter, likely through metal cation bridges, is favoured in alkaline extracts. This latter process is likely to be of greater significance in the examination of P sorption processes when P is added to basic residues.

With the exception of the Droogdam residue, the quantity of P present in non-labile Ca forms was low relative to other fractions (Table 2.2). It is likely that extensive precipitation of P-rich solid phases is inhibited by competing adsorption reactions (Dayton, 1995) and inherently low P contents. The positive correlation between HCl extractable P and Ca content ($r = 0.76$) (Appendix 2.3) does, however, suggest an association between P and Ca, although the mechanism of retention remains unclear. It was noted that the labile P fractions (bicarbonate and hydroxide extracts) tended to increase with an increase in Ca content even though it is expected that P concentrations would decrease with an increase in Ca content due to solid-phase precipitation. This suggests that a proportion of inherent labile P is retained on Ca mineral surfaces through weak forces of attraction as opposed to surface precipitation or specific sorption processes.

Residual P ranged from 41.9 to 60.9 % (Table 2.2) and represented the largest fraction of the inherent P in most of the residues. This fraction is expected to be comprised of inorganic and organic P strongly chemisorbed to mineral surfaces or occluded within mineral structures and is considered 'fixed' and not available for plant uptake. The P sorbed to amorphous Al and Fe oxides (19.4 to 93.8 %) (Table 2.2) reflects the addition of varying quantities of Al and Fe coagulants during the different treatment processes. The P sorbed to these oxide fractions comprises a significant fraction of total inherent P. It is difficult to determine from which fraction the oxalate extractable constituent is drawn without knowledge of amorphous Al and Fe distribution although most oxalate P is expected to be extracted from the residual fraction. The implication in cases where oxalate P is greater than residual P (e.g. Blackheath and Noditgedagt residues) (Table 2.2) is that ammonium oxalate has extracted P from sources other than the residual P fraction. This could be

attributed to amorphous Al and Fe oxides entrained or entrapped within the organic matter component. In fact, elevated P_0 values may well be attributed to P sorption by amorphous Al and Fe oxides within this component.

2.4 General Discussion and Conclusions

The characterisation of these 15 WTRs has shown a high degree of variability in the chemical properties relevant to P sorption and desorption processes. The use of specific treatment chemicals in varying quantities to treat raw water sources, which have their own distinctive characteristics, means that each residue has unique chemical properties. Phosphorus sorption processes should, therefore, be residue specific. The extent to which P is retained or released by WTRs will nonetheless be extensively influenced by a few important composition variables. Amorphous Al and Fe oxide in particular, have been shown to be strongly correlated to P sorption capacity (Dayton, 1995; Haustein *et al.*, 2000; Yang *et al.*, 2006) while high Ca contents favour the precipitation of insoluble calcium phosphates (Dayton, 1995). Phosphorus saturation indices have also been shown to give a good indication of P-fixing potential, particularly in Al and Fe based residues (Elliott *et al.*, 2002). It follows, therefore, that based on chemical characterisation data, all residues would be expected to adsorb high amounts of P. Furthermore, elevated amorphous Al and Fe and Ca contents suggest that sorbed phosphorus will be retained in forms unavailable for plant uptake.

Chemical fractionation revealed that most of the P in the WTRs was present in forms that were not available for plant uptake. While total P values were comparable to typical soils, most P was bound in non-labile organic or residual forms. This, in conjunction with their elevated quantities of reactive Al and Fe oxides (Section 2.3.1), suggests that plants growing on WTR amended soils may be subjected to growth inhibiting P deficiency. While this has been confirmed by numerous studies involving pot experiments (Bugbee and Frink, 1985; Cox *et al.*, 1997; Hyde and Morris, 2000), studies by Elliott *et al.* (1990a), Basta (2000) and Hughes *et al.* (2005), have shown that under field conditions, P deficiencies are not observed. In fact Hughes *et al.* (2005) noted that ryegrass grown on WTR amended soil showed no indication of P deficiency even though the grass roots were concentrated within the mulched layer. This suggests that this residue has sufficient P to satisfy plant growth requirements even though labile P fractions were below adequate soil levels. The high amount of P present in organically bound forms is, in this regard, of particular interest. It is possible

that the absence of P deficiencies under field conditions could be attributed to the gradual mineralisation of this fraction. In addition to this, plants may themselves increase labile P pools through disequilibria and ligand desorption mechanisms (Chapter 4).

While results from work by Hughes *et al.* (2005) and others are promising, variation in inherent P distribution means that agronomic applications of WTRs should be treated independently. Residues with low amounts of labile P (e.g. Voelvlei residue) may, for example, require P treatment prior to application. This is in contrast to residues with elevated plant available P (e.g. Droogdam) which may be applied directly to land. Ultimately, the success of land application needs to be assessed for each residue on a field scale. From an environmental context, the stability of the inherent P component is highly favourable and suggests that land application will not be negatively impacted by the excess surface runoff or leaching of P. In addition to this the high P sorption potential (low PSI values and elevated Ca content) of a number of residues (e.g. Blackheath and Faure residues) makes them suitable for use as eutrophication preventatives.

CHAPTER 3

SORPTION OF PHOSPHORUS BY WATER TREATMENT RESIDUES

3.1 Introduction

The ability of water treatment residues (WTRs) to sorb and retain plant available phosphorus (P) is a key issue with respect to the disposal of WTR by land application. Although numerous studies have documented the magnitude and consequences of such effects in agricultural (e.g. Hyde and Morris, 2000; Elliot *et al.*, 1990a; Hughes *et al.*, 2005) and environmental contexts (e.g. Macks *et al.*, 1998; Gallimore *et al.*, 1999; Elliot *et al.*, 2002), few have focussed on the chemical processes or mechanisms relating to P adsorption. Insight into the nature and relevance of these mechanisms is of fundamental importance if WTRs are to be disposed of efficiently.

The two methods used to quantify sorption processes include non-mechanistic (Section 1.4.1) and mechanistic (Section 1.4.2) techniques. Non-mechanistic techniques are based on the mathematical relationship between the equilibrium surface excess (S) (amount of a compound adsorbed) and the equilibrium solution concentration (c) of the compound. Mechanistic techniques, on the other hand, provide quantitative evidence to support the occurrence of a particular adsorption mechanism and are based on relating the equilibrium surface excess (S) to a solution property other than substance concentration (Essington, 2004). Most studies involving sorption of P by WTRs include non-mechanistic characterisation and a qualitative description of sorption processes (e.g. Hughes *et al.*, 2005). Few have, however, utilised non-mechanistic and mechanistic techniques in conjunction to quantitatively define P sorption processes. Those which have (Boisvert *et al.*, 1997; Ippolito *et al.*, 2003; Yang *et al.*, 2006) suggest that retention mechanisms are variable and closely related to the chemical properties of the sorbent. The aim of this study is to characterise the P sorption behaviour of 15 South African WTRs and to determine, using mechanistic and non-mechanistic techniques, the mechanisms responsible for the retention of P by the residues. The study has two parts: In the first part, the applicability of four empirical isotherm equations (Linear, Langmuir, Freundlich and Temkin) used to describe the sorption data and predict sorption behaviour, are tested. Non-mechanistic interpretation is carried out with respect to the assumptions from which the models are

derived. In the second part, the distribution of P sorbed to selected residues is determined by sequential fractionation. This fractionation data is utilised in a mechanistic context to corroborate or refute non-mechanistic assumptions.

3.2 Materials and Methods

3.2.1 Adsorption Isotherms and Modelling

Given the agronomic relevance of WTR-P sorption processes and the apparent contradiction between field and laboratory studies, the focus of this study is on processes relevant to the agricultural utilisation of WTRs. Phosphorus concentrations used in this experiment are thus based primarily on agronomically relevant ranges (0 to 32 mg P L⁻¹). In addition to this, P sorption measurements are based on the initial fast, reversible sorption step as opposed to the slower, sustained absorption phase. A contact time sufficiently long enough for equilibrium to be achieved but short enough to prevent slow deposition processes was subsequently chosen (i.e. 18 hours) (McGechan, 2002).

Phosphorus adsorption isotherms were determined for 15 South African WTRs using a method adapted from Hughes *et al.* (2005). Phosphorus was sorbed onto duplicate WTR samples by adding 1 g of WTR and 25 ml of a range of P solutions (0, 2, 4, 8, 16, 32, 64 and 128 mg P L⁻¹ as oven dried KH₂PO₄) to 50 ml polyethylene centrifuge tubes. Samples were shaken on an end over end shaker for 18 hours, centrifuged at 3500 rpm for 10 minutes and filtered through Whatman No. 42 filter paper into plastic vials. Phosphorus in the supernatant solution was determined colorimetrically by the molybdate blue method (Murphy and Riley, 1962) using a UV/visible spectrophotometer (Genesys 20 Thermo Scientific). The pH of the supernatant solutions was measured using a Meter Lab PHM 210 pH meter with a standard glass electrode.

Adsorption isotherms were constructed by plotting the quantity of P adsorbed against the residual P concentration. Adsorbed P was calculated as the difference between the initial P and residual P concentrations, and related to the mass of sample used. The data analysis software Graphical Analysis 3.0 (Vernier Software and Technology, 2002) was used to test the applicability of four empirical adsorption isotherm equations (Langmuir, Freundlich, Temkin and linear) to describe the adsorption data (Table 3.1). The equation yielding the highest correlation coefficient during linear

transformation was chosen for use. A more thorough explanation of these models and their applicability is given in Section 1.4.

Table 3.1 Empirical isotherms equations used to describe P adsorption data in conjunction with linearizing transformations used for parameter determination

Model	Equation ^a	Linear Transformation			
		Equation	Plot	Slope	Intercept
Langmuir ^b	$S = K.c.x_m/(1 + K.c)$	$c/S = c/x_m + 1/x_m K$	c/S vs c	$1/x_m$	$1/x_m K$
Freundlich ^c	$S = K.c^a$	$\log S = a.\log c + \log K$	$\log S$ vs $\log c$	a	$\log K$
Temkin ^d	$S = K_1.\log(K_2.c)$	$S = K_1.\log c + K_1.\log K_2$	S vs $\log c$	K_1	$K_1.\log K_2$
Linear ^e	$S = K_d.c + a$	$S = K_d.c + a$	S vs c	K_d	a

^a S and c represent the quantity of P adsorbed (mg kg⁻¹) and the residual P concentration (mg L⁻¹) respectively.

^b K and x_m represent the affinity parameter and the maximum adsorption per unit mass respectively.

^c K is the distribution coefficient and a is a correction factor relating to the heterogeneity of adsorption sites.

^d K₁ and K₂ are parameters.

^e K_d and a are the distribution coefficient and y intercept respectively.

3.2.2 Phosphorus Fractionation

The distribution of P sorbed to seven WTRs (Randwater, Faure, Blackheath, Loerie, Bloemfontein, Midmar and Nahoon) was determined by a method adapted from Zhang and Mackenzie (1997) (Section 2.2.3). These residues were selected for further study due to the range of sorption behaviours and also because four of them (Randwater, Faure, Bloemfontein and Midmar) represented the major South African water treatment plants. Prior to fractionation, duplicate samples (0.5 g WTR in 50 ml polyethylene centrifuge tubes) were allowed to adsorb P (as oven dried KH₂PO₄) from 25 ml of solution to give residual P concentrations falling within the predictive ranges of the fitted models (Section 3.3.2). The sorption process was the same as used for the determination of the isotherm data (Section 3.2.1). The concentration of P in the supernatant solution was determined colorimetrically by the molybdate blue method (Murphy and Riley, 1962) and compared to the concentrations predicted by the respective models. The P fractionation was carried out as described in Section 2.2.3.

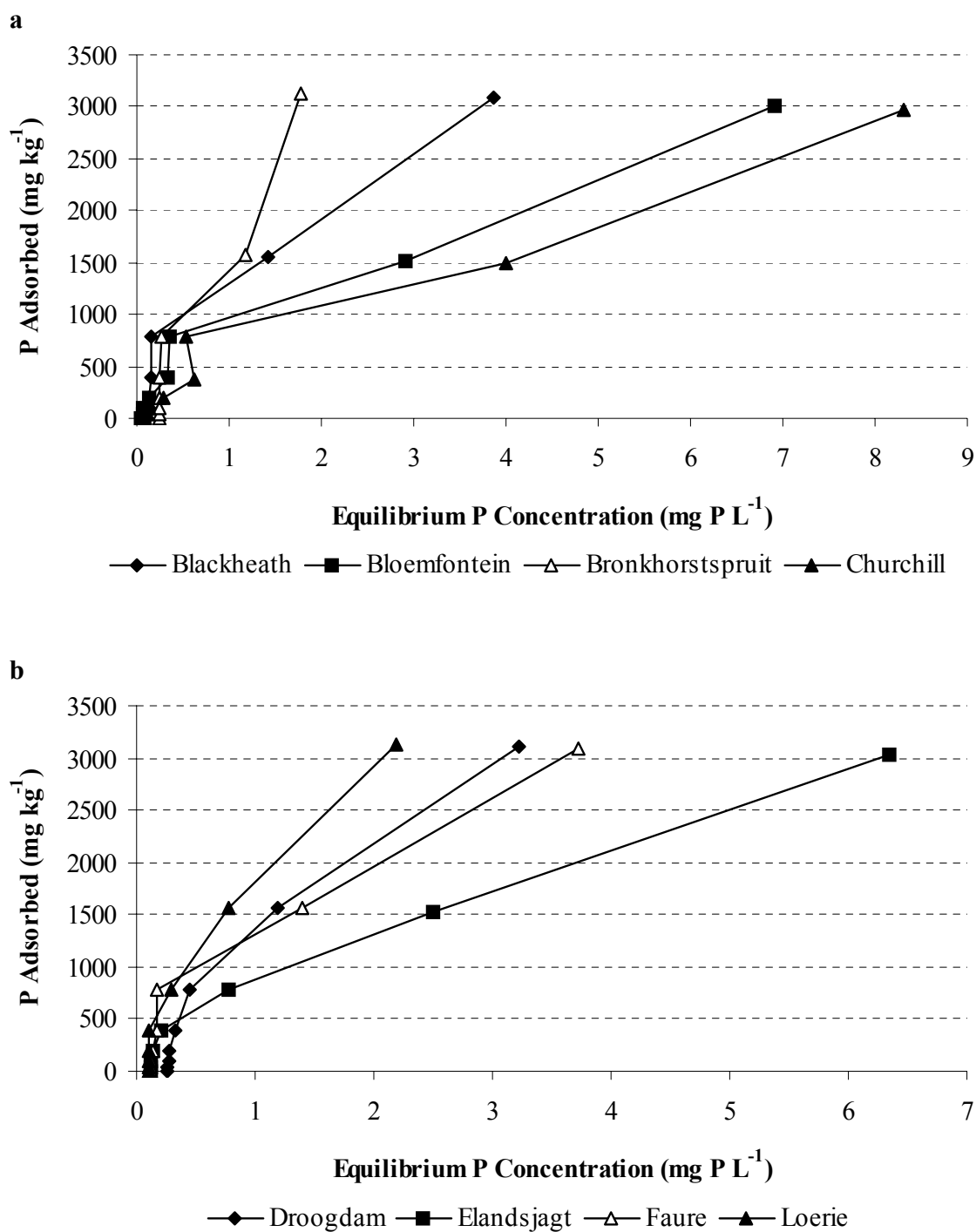
3.2.3 Oxalate Extractable Phosphorus

Phosphorus bound to noncrystalline or poorly ordered Al and Fe oxides was determined after an acid ammonium oxalate extraction (Loeppert and Inskeep, 1996). Phosphorus extracted during the inorganic sequential fractionation step was considered to be bound mostly to crystalline Al and Fe hydroxide surfaces (Bayley *et al.*, 2008). As in Section 3.2.2, P was sorbed to 0.5 g of residue to give residual P concentrations within the required agronomic ranges which were then compared to the concentrations predicted by the respective models. Following extraction, samples were centrifuged at 3500 rpm for 10 minutes and analysed for Al, Fe, Ca and P using ICP-AES. All extractions were carried out in duplicate.

3.3 Results and Discussion

3.3.1 Phosphorus Adsorption Isotherms

The 15 WTRs characterised in this study demonstrated a range of sorption behaviours (0 to 128 mg P L⁻¹; Figures 3.1, 3.2, 0 to 32 mg P L⁻¹ range; Appendix 3.1) which suggests a variety of interactions between P and the sorbing components. Sorption capacities were marked with most of the residues retaining greater than 95 % of applied P at all application rates between 2 and 128 mg P L⁻¹ (Appendix 3.2). Similar to the findings of Hughes *et al.* (2005), P adsorption appeared to take place in a step-wise manner (e.g. Bloemfontein and Churchill, Figure 3.1 a), although this was not evident for all residues, probably due to the limited P concentration range. All residues retained similar quantities of P at the highest application rate (128 mg P L⁻¹) suggesting that maximum P sorption capacities had not yet been reached. At residual P concentrations of between 0.5 and 8 mg P L⁻¹, P adsorption tended to increase in a linear manner without reaching any noticeable sorption maximum (Figures 3.1 and 3.2). At lower concentrations (0 to 0.5 mg P L⁻¹), the sorption isotherms were characterised by steep slopes (Appendix 3.1), a characteristic that suggests strong sorbate-sorbent interactions. Holford (1989) noted that the slope of a sorption isotherm gives an indication of the capacity of the sorbent to sorb or fix a quantity of sorbate, or to buffer solution concentrations. In the context of this study, this reflected the equilibrium between P bound to the residue and that in solution. Therefore steep slopes, as seen for most of the WTRs, suggest that P is tightly bound to the residue surface and is not readily released into solution.



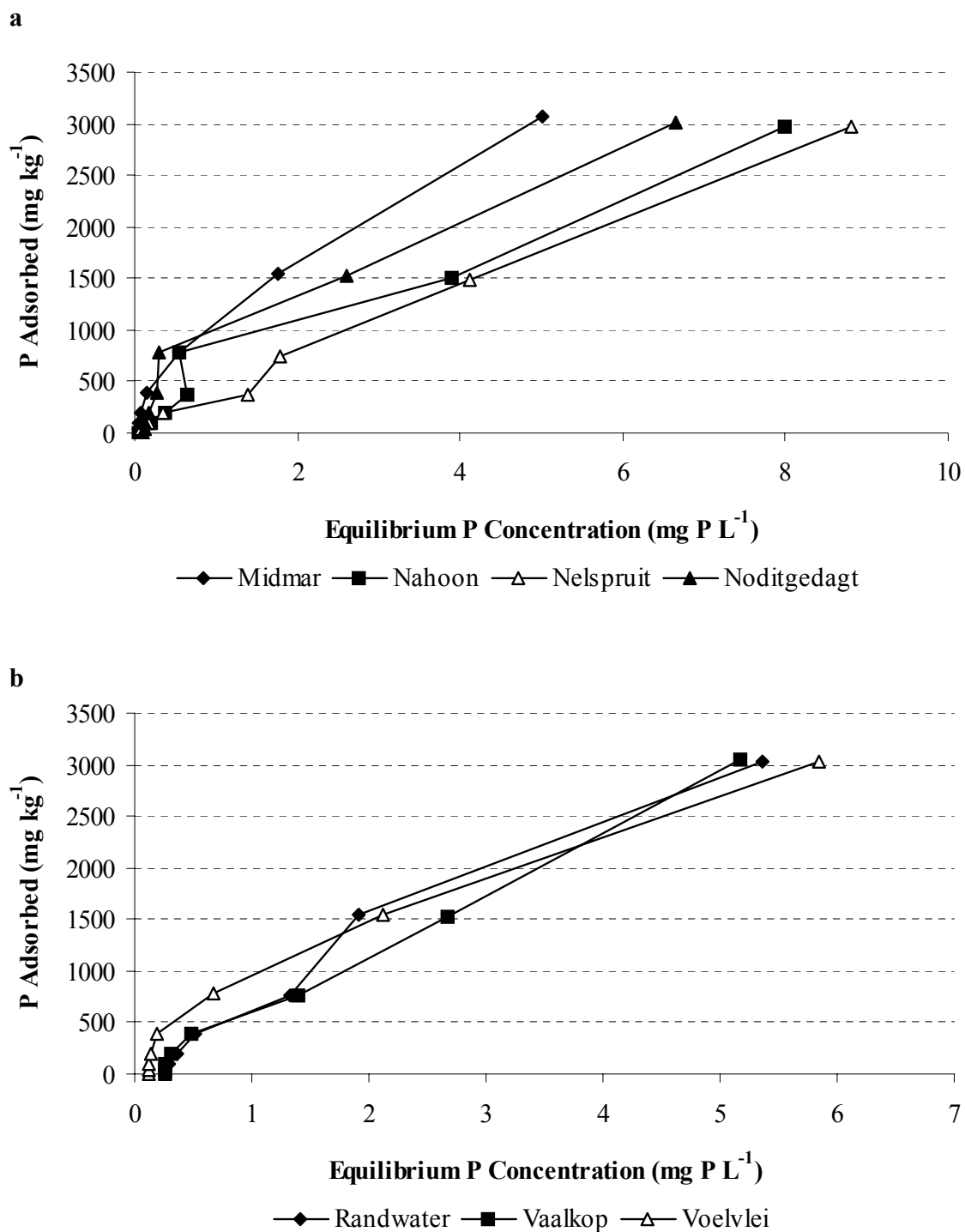


Figure 3.2 Phosphorus adsorption isotherms for (a) Midmar, Nahoon, Nelspruit and Noditgedagt and (b) Randwater, Vaalkop and Voelvllei water treatment residues at P applications of between 0 and 128 mg P L⁻¹. The sorption isotherms of these residues at P applications between 0 and 32 mg P L⁻¹ are given in Appendix 3.1.

A residual P concentration of 0.20 mg L^{-1} is often considered as the optimum concentration of P in the soil solution required for plant growth (Fox and Kamprath, 1970) although lower values have been proposed which are generally plant and soil specific (Hughes *et al.*, 2005). It is evident that the ability of WTRs to supply plants with P varies markedly (Table 3.2). To give an indication of the amount of fertiliser P required to achieve residual solution P concentrations of 0.50 , 0.20 and 1.0 mg L^{-1} , the equivalent amount of single super-phosphate required to achieve these values was calculated. This was achieved based on an assumed WTR bulk density of 1200 kg m^{-3} and a residue application depth of 10 cm .

Table 3.2 The amount of sorbed P required to achieve residual P concentrations of 0.05 , 0.20 and 1.0 mg L^{-1} for 15 South African water treatment residues and the equivalent amount of superphosphate to be added to achieve this

Sample	Amount of P sorbed to achieve the residual P values (mg L^{-1}) indicated ^a					
	0.05 ^b		0.20 ^c		1.00 ^d	
	mg kg^{-1}	SPE	mg kg^{-1}	SPE	mg kg^{-1}	SPE
Blackheath	0	0	826	4356	1305	6881
Bloemfontein	4.85	26	253	1334	973	5131
Bronkhorstspuit	0	0	0	0	1417	7472
Churchill	0	0	129	680	877	4625
Droogdam	0	0	0	0	1357	7156
Elandsjagt	0	0	358	1888	886	4672
Faure	0	0	805	4245	1309	6902
Loerie	0	0	599	3159	1025	5405
Midmar	110	580	445	2347	1071	5647
Nahoon	2.33	12	95	501	884	4661
Nelspruit	0	0	110	580	298	1571
Noditgedagt	0	0	264	1392	1015	5352
Randwater	0	0	0	0	615	3243
Vaalkop	0	0	0	0	599	3159
Voelvlei	0	0	400	2109	949	5004

^a Values determined by extrapolation off the isotherms (Figures 3.1 and 3.2).

^b Zupancic (1996). ^c Fox and Kamprath (1970). ^d Hughes *et al.* (2005).

SPE Super Phosphate Equivalent ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) (kg ha^{-1}).

Thus for the Midmar residue, the application of $110 \text{ mg P kg}^{-1} \text{ P}$ (0.05 mg P L^{-1} residual) is equivalent to applying 580 kg of super-phosphate to a depth of 10 cm over an area of one hectare. Of particular interest was that at residual P concentrations of 0.05 mg P L^{-1} almost all of residues (with the exception of Bloemfontein, Midmar and Nahoon) released sufficient P without the need for further addition of P. At higher residual P values (0.2 and 1 mg P L^{-1}) most of the WTRs required P to be added for sufficient residual P concentrations to be achieved, and in some instances (e.g. Blackheath and Faure) considerably higher amounts of added P were required than the other WTRs.

The implication is that there is sufficient inherent labile P within these residues to maintain low concentrations of residual P in solution (i.e. inherent P is released or desorbed from the residues). A key point, however, is that the buffer capacity gives no indication of replenishment capacity. So while equilibrium P concentrations were, for some residues, above those required for optimum plant growth, the lack of P in exchangeable forms (Section 2.3.2) will in all likelihood place a limit on the quantity of P available for plant uptake. Given that a minimum of 0.05 mg P L^{-1} was available for release from most of the residues is, nevertheless encouraging from an agronomic perspective and could explain, at least in part, why P deficiencies are absent under field conditions.

3.3.2 Modelling

Of the 15 WTRs, sorption data for 10 of the residues was described by the Temkin isotherm while the Freundlich and linear models fitted data for two residues each. No model was found to fit sorption data derived from the Loerie residue (Table 3.3). Because of the step wise nature of adsorption, models tended to be applicable within a restricted concentration range, typically between P additions of 0 and 32 mg L^{-1} . Residues demonstrating ‘smooth’ parabolas (e.g. Midmar) were, however, described over a broader range of P concentrations. In the case of the Voelvlei residue, the applicability of the Temkin isotherm, over a wide concentration range, meant that it was chosen for use even though the Freundlich model gave a slightly higher correlation coefficient (Appendix 3.3). The R^2 values for the respective models were in all cases over 0.93, with most over 0.95, indicating a close mathematical relationship between model parameters and sorption derived data. The high correlation coefficients have two major implications in the context of P sorption investigations. Firstly, the applicability of a particular empirical adsorption isotherm suggests that the assumptions from which the model was derived are relevant. Sorption models may, in this regard, be used in the

mechanistic interpretation of sorption processes. They should, however, be viewed purely as an aid as they are often only mathematical descriptions of macroscopic data (Sparks, 1995). Secondly, the accurate description of sorption data allows for the prediction of quantity-intensity relationships within a given concentration range. This is useful from both an agronomic and an environmental perspective given the close relationship between residual P and plant growth. The utilisation of the fitted models for predictive purposes is discussed in Section 3.3.5.

Table 3.3 Empirical sorption equations used to describe the adsorption of P by 15 South African WTRs

WTR	Best Fit Model	Equation	Residual P Range (mg L ⁻¹) ^a	Parameters		R ²
				Slope (Affinity Parameter)	Intercept/constant	
Blackheath*	Linear	$S = K_d \cdot c + a$	0.112 – 0.161	$K_d = 8072$	$a = -908$	1.00
Bloemfontein*	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.046 - 0.340	$K_1 = 444$	$K_2 = 21.5$	0.998
Bronkhorstspuit	Freundlich	$S = K \cdot c^a$	0.249 - 0.252	$K = 3.39 \times 10^{134}$	$a = 220$	0.995 ^b
Churchill	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.096 - 0.615	$K_1 = 434$	$K_2 = 11.2$	0.973
Droogdam	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.264 - 0.455	$K_1 = 4470$	$K_2 = 3.83$	0.977
Elandsjagt	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.112 - 2.508	$K_1 = 887$	$K_2 = 10.7$	0.979
Faure *	Linear	$S = K_d \cdot c + a$	0.115 – 0.161	$K_d = 7726$	$a = -897$	0.999
Loerie *	None	-	-	-	-	-
Midmar*	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.037 - 0.544	$K_1 = 651$	$K_2 = 29.2$	0.996
Nahoon*	Freundlich	$S = K \cdot c^a$	0.102 - 0.654	$K = 599$	$a = 1.12$	0.999
Nelspruit	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.103 - 1.39	$K_1 = 287$	$K_2 = 13.1$	0.963
Noditgedagt	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.110 – 0.272	$K_1 = 981$	$K_2 = 9.39$	0.993
Randwater*	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.253 - 1.32	$K_1 = 1058$	$K_2 = 4.17$	0.991
Vaalkop	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.253 - 0.479	$K_1 = 1302$	$K_2 = 4.25$	0.935
Voelvlei	Temkin	$S = K_1 \cdot \log(K_2 \cdot c)$	0.112 - 0.675	$K_1 = 955$	$K_2 = 10.6$	0.950
Al-oxide ^c	Linear	$S = K_d \cdot c + a$	0 - 0.003	$K_d = 1755$	-	0.960
Avalon soil ^d	Temkin	$S = K_1 \cdot \ln(K_2 \cdot c)$	0.025 - 2.10	$K_1 = 57$	$K_2 = 24.4$	-
Avalon soil ^d	Freundlich	$S = K \cdot c^a$	0.025 - 2.10	$K = 219$	$a = 0.549$	-

^a This represents the residual P range for which the respective models were applicable.

^b An R² value for the Bronkhorstspuit curve was not obtained. This R² value is from the linear transformation.

^c Al₂O₃ (Leader *et al.*, 2008). ^d Henry and Smith (2005).

* These residues were chosen for further study.

Central to the interpretation of empirical adsorption isotherms is the distribution coefficient (K_d). This term is related directly to the bonding energy of the adsorbing surface and is expressed as the ratio of S to c at a given application concentration (Hinz, 2001). Different models base their assumptions on the relationship between K_d and S . In the Langmuir isotherm, K_d is assumed to be constant and that the affinity of the adsorbate for the adsorbent is independent of the number of occupied adsorption sites (Travis and Etnier, 1981). In the Freundlich and Temkin models K_d is assumed to be a decreasing exponential and decreasing linear function of S , respectively. Plotting K_d against S (a Scatchard plot; Kinniburgh, 1986) is, therefore, useful to determine whether the assumptions from which a particular model were derived are relevant for a set of sorption data (Figure 3.3). At application concentrations of between 0 and 32 mg P L⁻¹, K_d increases with P sorbed for all WTRs except for the Nelspruit residue (Figure 3.3). This relationship contradicts the central assumptions of the Freundlich and Temkin models and highlights the point that isotherm equations should be viewed as empirical until corroborating data is available to support the assumptions. Although model assumptions were more applicable at higher concentrations (32 to 128 mg P L⁻¹), as seen in declining or constant K_d values, acceptable correlation coefficients were, in general, only obtained at P additions of between 0 and 32 mg P L⁻¹ (Appendix 3.3). This range was considered satisfactory given the agronomic focus of the study. So while the mechanistic interpretation of these isotherms does not necessarily match those of the model assumptions, P sorption processes may be qualitatively assessed by examining the derived model parameters (Table 3.3) and variations in K_d (Figure 3.3). In terms of the Langmuir model, deviations from the isotherm may be attributed to the dependence of K_d on S . In this case one or more of assumptions on which the model is based do not hold true for P adsorption to WTRs, which includes:

1. adsorption may well proceed beyond monolayer coverage,
2. all sites are not equivalent and the surface is not uniform, and
3. the ability of a molecule to adsorb at a given site is dependent or is influenced by the occupation of neighbouring sites (Section 1.4.1.2).

Given the chemical heterogeneity of these residues, it was expected that the R^2 values for the Langmuir linearising transformations would be well below those of the other models examined (Appendix 3.4).

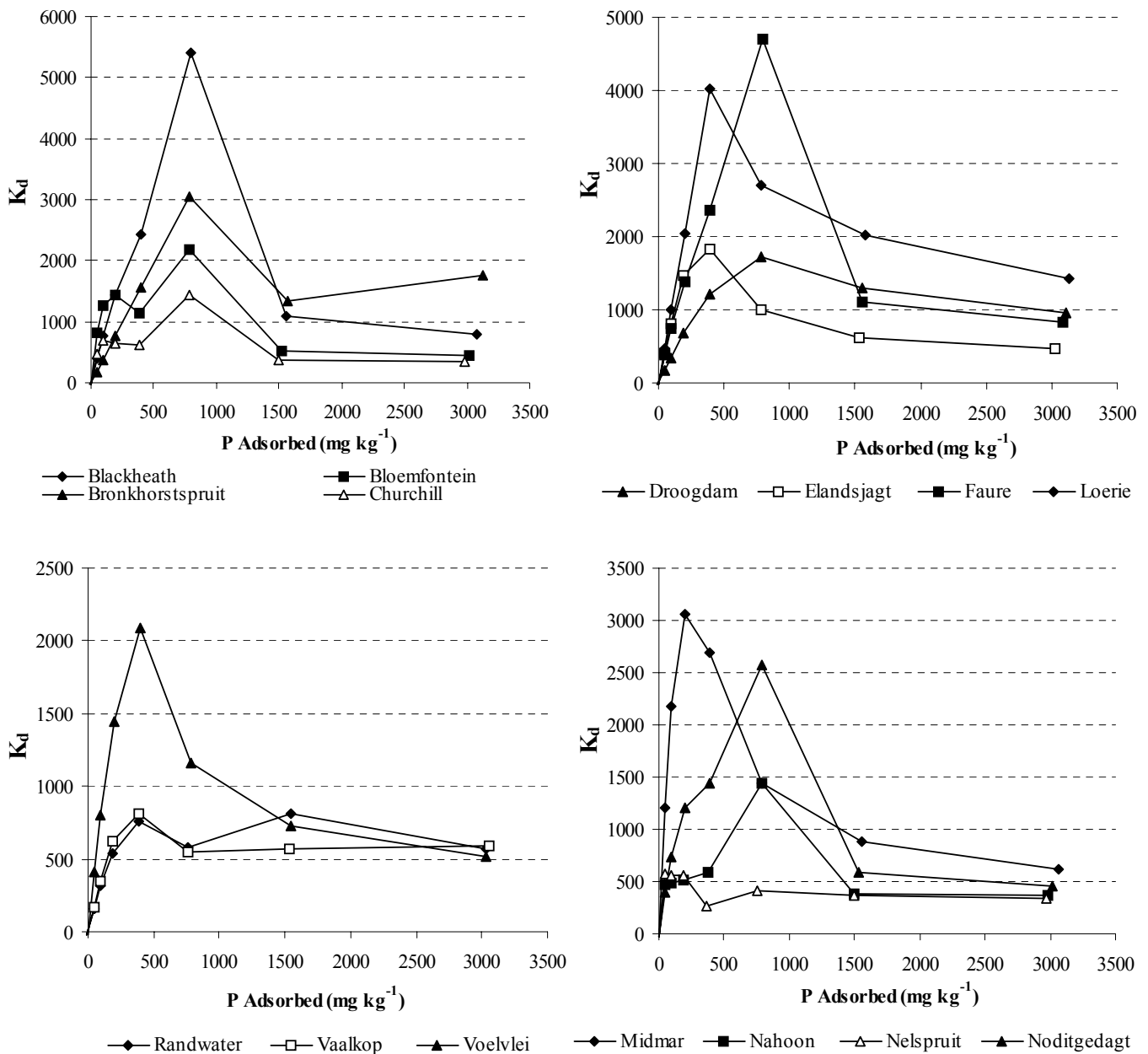


Figure 3.3 Scatchard plots for 15 South African WTRs showing the relationship between the distribution coefficient and the quantity of P adsorbed. K^d refers to the distribution coefficient (S/c).

The fact that the sorption data was described by the linear, Freundlich or Temkin isotherms, indicates that the affinity of the adsorbate for the adsorbent is dependent on the quantity of P adsorbed. It is evident that at concentrations relevant to agronomic applications (0 to 32 mg P L^{-1}), K_d is generally an increasing linear function of S . This explains why the models derived from linear assumptions (linear and Temkin isotherms) provided accurate descriptions of the sorption data. For

those residues for which the Freundlich isotherm was applicable, K_d was shown to be a logarithmic function of S , although the proximity of the constant a to one in the Nahoon residue suggests a near linear association. The implication for these residues is that the affinity of the adsorbent surface for P increases up to an apparent threshold concentration (16 to 32 mg $P\ L^{-1}$), suggesting that the enthalpy of adsorption becomes more negative. This implies an activation of sorption sites and suggests that the energetically most favourable sites are only occupied once a certain base level of sorption has been attained (Atkins and de Paula, 2002). Once high affinity sites are saturated, K_d then decreases or remains constant in accordance with respective Freundlich, Temkin and Langmuir model assumptions. In the case of the Blackheath and Faure residues, conformity to the linear model suggests that S is independent of the occupation of sorption sites. This linear association may, however, simply indicate that the quantity of sorption sites far exceeds the quantity of P applied. This is corroborated by K_d values which were considerably greater than for the other residues (Table 3.3).

Given that these data do not appear to meet the assumptions of the Temkin and Freundlich models, these models cannot be used for mechanistic purposes. Sorption processes may, however, be quantified by examining the relationship between parameter values and WTR properties. Parameter values for the respective models were divided into two general groups, specifically those referring to the slope (affinity parameter) and those referring to the intercept or constant of the respective empirical isotherm equations (Table 3.3). Because affinity parameter provide a quantitative measure of the reactivity of the sorbent surface, high values (e.g. Droogdam) indicate strong sorbate-sorbent interactions while lower values (e.g. Churchill) suggest sorption is inhibited. Values obtained for the WTRs were greater than those obtained for typical soils over similar concentration ranges (Table 3.3), a feature attributed to elevated quantities of reactive amorphous Al and Fe oxides.

Affinity parameters varied considerably (Table 3.3) which suggests that the reactivity of the sorbent is dependent on an intrinsic property of residue. To investigate the relationships between model parameters and WTR chemical properties, a correlation matrix was produced (Appendix 3.4). For those residues described by the Temkin equation, K_1 was found to be positively correlated to exchangeable Ca and oxalate extractable Fe but not to oxalate extractable Al nor to dithionate or pyrophosphate Al and Fe. On closer inspection, however, it was evident that affinity parameter values were, for all models, correlated to the sum of dithionate extractable Al and Fe ($R^2 = 0.784$) when residues with high organic carbon contents were omitted (Figure 3.4).

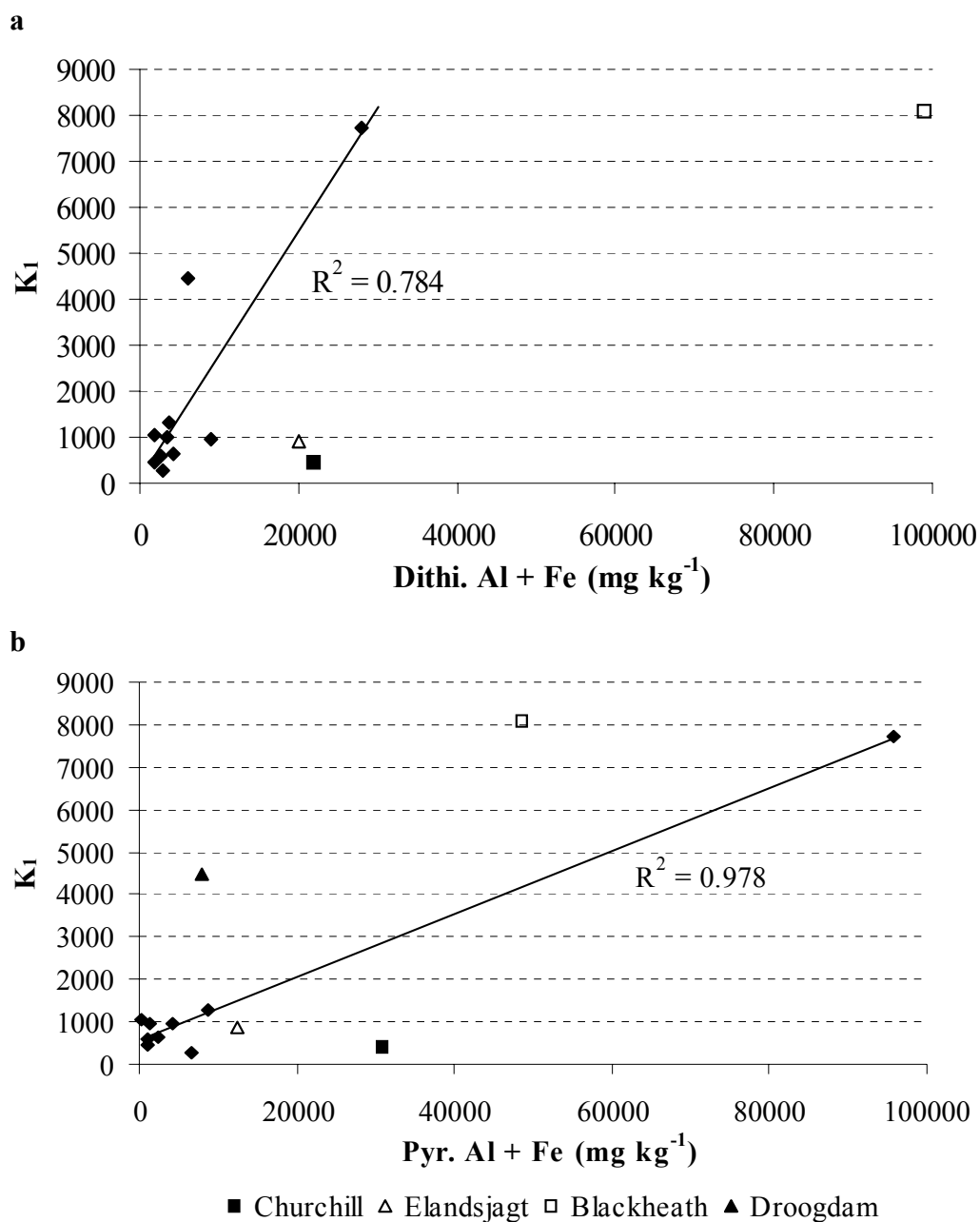


Figure 3.4 Relationship between affinity parameters and the sum of (a) dithionate extractable Al and Fe (Dithi. Al + Fe) and (b) pyrophosphate extractable Al and Fe (Pyr. Al + Fe) for the P sorption data of 13 South African WTRs described by the Temkin, Freundlich and Linear models. Data for the Bronkhorstpruit and Loerie residues are not presented.

Values tended to be lower in residues with high organic carbon contents, possibly due to the masking of sorption sites by the organic component. A similar relationship was obtained between

the affinity parameters and the sum of pyrophosphate extractable Al and Fe ($R^2 = 0.978$), although a strong correlation was only obtained when values from the Droogdam residue were omitted (Figure 3.4). The implication for those residues with elevated affinity parameter values (Droogdam and Elandsjagt) is that sorption is enhanced by a property other than organically bound Al and Fe. In the Droogdam residue, this may be attributed to an elevated Ca content (Section 2.3.1). Therefore, the affinity of the WTR surface for P and hence the magnitude of sorption is, for most of residues, dependent on the total quantity of free Al and Fe oxides which includes exchangeable Ca, oxalate extractable Fe and organically bound Al and Fe. Although affinity parameters were strongly correlated to organically bound components, the slope of this linear regression (0.075) was less than that obtained from the dithionate extraction (0.267). This suggests that the total ‘free’ Al and Fe oxide content has a greater impact on the magnitude of sorption than organically bound Al and Fe. Of additional interest are the correlations between affinity parameter values and inherent P fractions (Appendix 3.5). The inverse relationship between K_1 and P bound to organic fractions suggests that the magnitude of sorption is reduced by inherent P, presumably through the occupation of sorption sites. In contrast, affinity parameters were shown to be directly related to loosely held P and P associated with Ca. Thus in residues with a high affinity for P, a greater quantity of inherent P is retained in labile fractions rather than fixed to high affinity sites.

3.3.3 Phosphorus Fractionation

A key focus of this study was to determine the distribution of applied P within the respective WTR sorbing components. Prior to fractionation, P was sorbed to the selected residues to give residual P concentrations falling within the ranges predicted by the respective adsorption isotherm equations (Appendix 3.6). The sequential P fractionation (Section 2.2.3) identified soluble and loosely held P (bicarbonate extract), P bound to the surfaces of Al and Fe oxides (NaOH extract), Ca bound P (HCl extract) and P occluded within mineral structures (acid digest). Phosphorus present in organic forms was also identified and separated into respective bicarbonate and hydroxide fractions (Appendix 3.7). While data from this study suggests that WTR-P sorption processes are complex and highly specific, a number of general trends are present which supersede model specificity.

Plant available P, considered as the inorganic component extracted with bicarbonate and hydroxide (P_i), increased for all seven residues with the addition of P (Appendix 3.8). Condron *et al.* (2005) have noted that inorganic fractions may be underestimated during fractionation procedures (Section

2.3.2) due to experimental error in colorimetric P determination steps. This, in conjunction with the tendency for orthophosphate to complex with organic matter in alkaline extracts, means that labile fractions were probably underestimated. The magnitude of this error is, however, likely to be small in relation to the quantity of P present in strongly sorbed or fixed fractions. The ability of plants to access labile pools is likely to be further restricted by continual sorption processes (Makris *et al.*, 2004b; Makris and Harris, 2006).

With the exception of the Faure residue, the quantity of P bound to Ca forms decreased with addition of P. The absence of any noticeable rise in Ca-P fractions suggests either that precipitation processes were inhibited, or that the concentration of extractant used to release Ca bound P (1 M HCl) may not have been of sufficient strength to dissolve highly insoluble Ca-P mineral phases resulting in an overestimation of residual fractions. Though this explanation is plausible, carbonate based sorbents apparently only contribute to sorption when they are dominant in soils (or, in this case, WTRs) and excess P is applied (Zhou and Li, 2001). A number of studies (e.g. Hamad *et al.*, 1992; Zhou and Li, 2001) have documented that calcium based minerals play a minor role in the sorption of P to calcareous soils. Phosphorus retention in these soils has been attributed primarily to noncarbonate clays and Al and Fe oxides bound to Ca-mineral surfaces. In the context of this study, the extensive formation of resistant Ca-P phases was likely to be limited by competing adsorption reactions (Dayton, 1995) and the low P concentrations (0 to 128 mg P L⁻¹). Furthermore it was found that P addition results in redistribution of inherent Ca bound P. Plots of pH against P adsorbed (Appendix 3.9) suggest that, prior to redistribution, P is released through desorption processes as opposed to mineral dissolution (within applied concentrations ranges, pH remained above 7 and tended to increase with P adsorbed). If this is the case, a proportion of Ca bound P is present in exchangeable forms though the quantity of P in this fraction is small and probably negligible.

For all residues, P application resulted in a noticeable increase in residual P contents (Appendix 3.8). The implication is that the majority of applied P is retained through strong chemisorption processes such as ligand exchange (Yang *et al.*, 2006) and intraparticle diffusion of P (Makris *et al.*, 2004b). In contrast, P bound to organic fractions decreased, in some cases notably (e.g. Blackheath and Nahoon), which confirms the occurrence of P redistribution processes. These variations in P distribution are summarised in Figures 3.5 and 3.6 which relate the percent change in P bound to a component (as a function of total P adsorbed) to the quantity of P adsorbed. For example in the Blackheath WTR (Figure 3.5 a), the retention of 303 mg P kg⁻¹ resulted in a 12 % increase in labile

P, a 120 % increase in residual P and a 41 % decrease in P bound to organic fractions. Unaccounted P refers to the fraction not extracted or accounted for during the sequential extraction. Negative values, therefore, indicate a net release of P after P addition while positive values suggest a proportion of sorbed P is retained in forms resistant to strong degrading reagents (e.g. concentrated H_2SO_4). The apparent redistribution of inherent P fractions is important as it suggests mechanisms of adsorption that involves the activation of sorption sites. The negative relationship between organically bound P and residual fractions (Figure 3.6) suggests that P application results in a transfer of P from relatively stable fractions (organic and Ca-bound) to highly stable forms (residual and unaccounted fractions). These data are in agreement with data obtained from the modelling study (Section 3.3.2) where the affinity of the WTR surface for P was shown to increase with the application of P. Therefore, the retention of P by WTRs appears to be closely related to the quantity of P applied and chemical properties of the sorbent, specifically organic matter content.

A mechanistic hypothesis is proposed to describe the redistribution of P as more P is added. It is based on the assumption that the initial fast reaction phase (Section 1.3.1) is controlled by the nature and reactivity of the sorbent surface. Prior to P application, WTR surfaces are coated by organic colloids. This organic component, comprised of hydrous Al and Fe oxides and Ca and Mg carbonates bound to long chain organic polymers and organic acids, regulates the surface reactivity of the residue. Phosphorus, which is added is, therefore, initially adsorbed or retained by the reactive organic component. As successive amounts of orthophosphate are sorbed by this 'pseudo' surface, the net charge of the organic component decreases. The organic matter-P complex is then consequently repelled by the predominantly negatively charged WTR surface and highly reactive hydrous Al and Fe sites are then exposed and the affinity of the WTR for P rapidly increases. This surface activation results in a redistribution process whereby applied and inherent P is transferred from labile pools to sites with a higher affinity for P. As high affinity sites are saturated, sites with successively lower complexation constants are occupied and labile P fractions gradually increase.

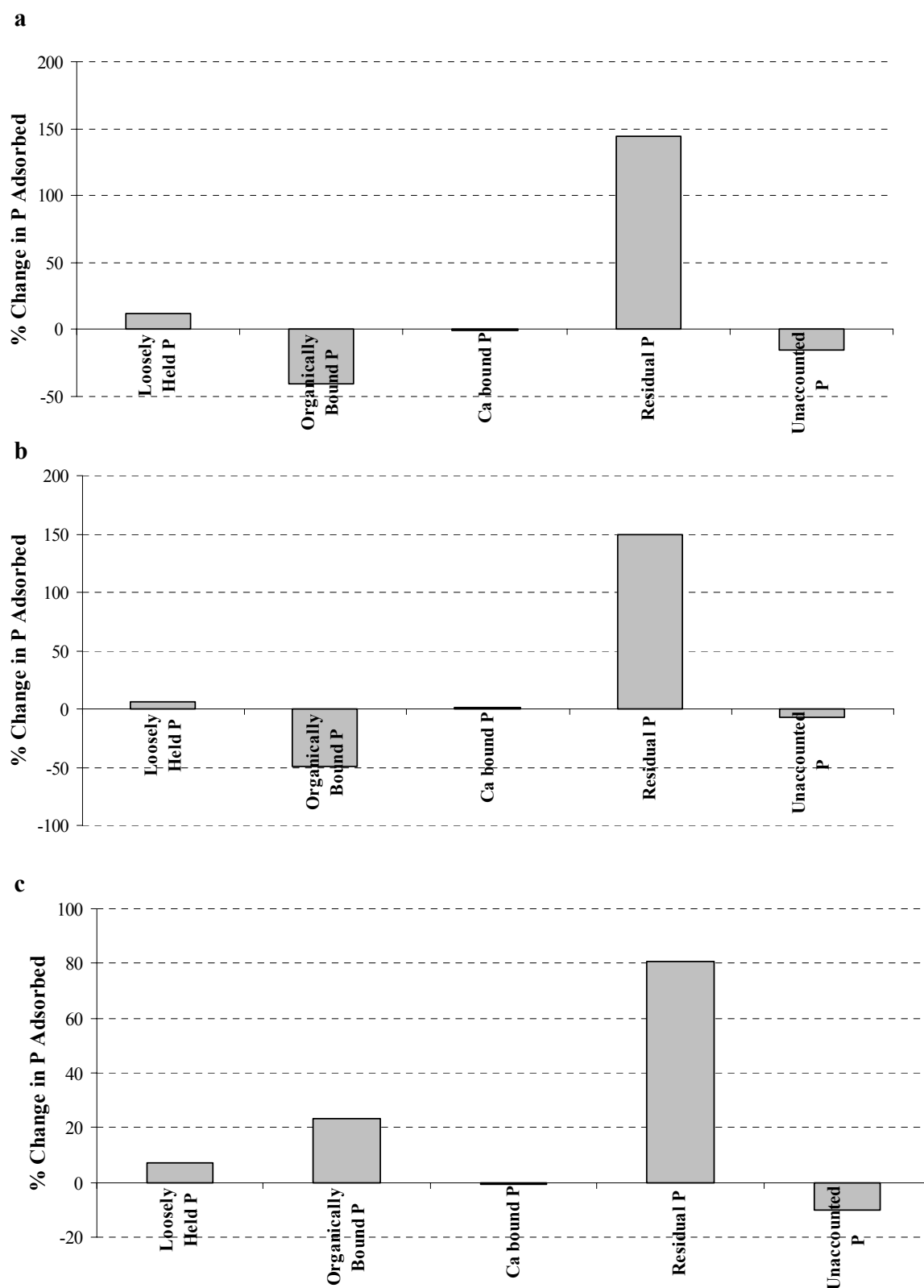


Figure 3.5 Change in the distribution of P within 0.5 g of (a) Blackheath, (b) Faure and (c) Loerie WTR after the application of 6.2, 5.4 and 4.1 mg P L⁻¹ respectively. The percentage change was calculated as: (Change in the quantity of P sorbed to a component / Total P sorbed) × 100.

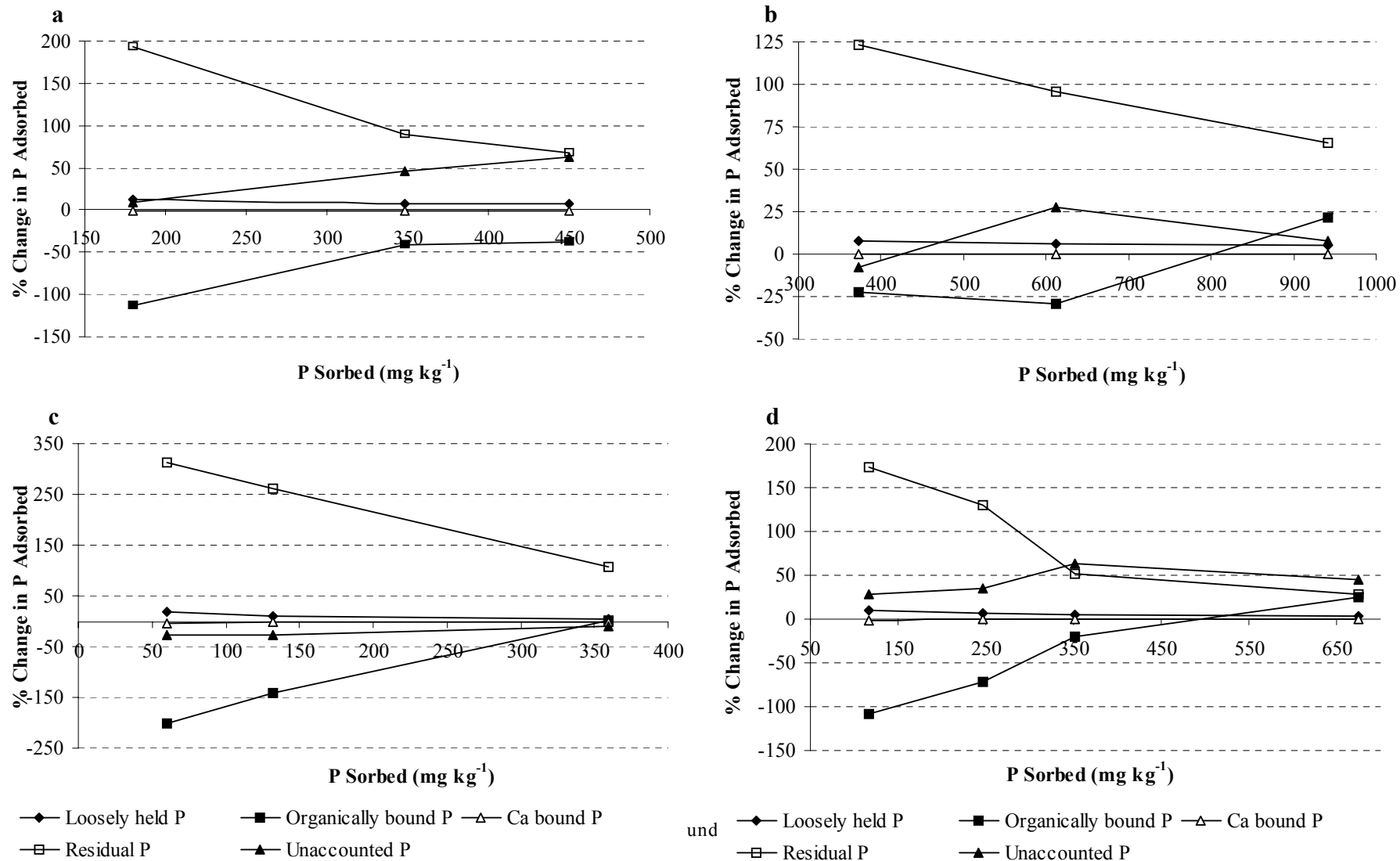


Figure 3.6 The percentage change in the distribution of P in the (a) Bloemfontein, (b) Midmar, (c) Nahoon and (d) Randwater WTRs relative to the quantity of P adsorbed.

This hypothesis is best supported by examining the residues which were fractionated at multiple additions of P (Figure 3.6). It is evident that percentage changes (∂P) for residual and organic P fractions are greatest at low concentrations and tend to decrease as P sorbed increases. It is suggested that at low values of applied P, sorption site activation results in marked P desorption from the organic fraction. As the amount of P added increases, a greater quantity of high affinity sites are occupied by the added P thus restricting desorption from the organic fraction. At higher concentrations, this fraction is then converted back to a P sink as high affinity sites are saturated resulting in the observed decrease in ∂P for the residual fractions. These declines for residual P tend to be balanced by concurrent increases in unrecovered P. So while the total quantity of P in inorganically fixed forms (residual P + unaccounted P) decreases with P sorbed, an increasing fraction of this P is presumably present in highly resistant mineral phases. Of particular interest is the observation that at P sorbed values greater than the point of maximum inflection on respective Scatchard plots (Figure 3.3), ∂P is positive for the respective organic fractions (Figure 3.6). This confirms the notion that sorption sites with the highest affinity for P are only occupied once a certain base level of sorption is achieved (Section 3.3.2), or desorption of P from the organic component ceases once sites with higher P complexation constants are saturated.

3.3.4 Adsorption Mechanisms

Both the modelling (Section 3.3.2) and fractionation studies (Section 3.3.3) strongly suggest that the adsorption of P by WTRs involves the activation of sorption sites and the subsequent redistribution of inherent and added P fractions. It is unclear, however, which mechanisms are responsible for the retention of P and whether similar mechanisms of adsorption are operative between residues. The chemical heterogeneity of WTRs implies that mechanisms will vary. This notion is confirmed by the pH against P adsorbed plots (Appendix 3.9), which indicate a unique pattern for every residue investigated. The similarity in K_d variation (Figure 3.3) and given that sorption data was generally described by the Temkin isotherm (Table 3.3) is, however, indicative of mechanistic similarity. So while the specific chemical processes of adsorption are complicated and highly variable, there are a few major mechanisms of retention which will generally exert a controlling influence on P sorption processes. Studies which have focussed on mechanisms of P retention by WTRs suggest that dominant mechanisms of retention include ligand exchange, charge neutralisation, proton transfer and precipitation reactions (Section 1.3.2). In this study, a lack of quantitative evidence to support

the occurrence of these mechanisms means that mechanistic interpretation may only take place on a qualitative basis through the examination of fractionation data.

Because sequential fraction procedures are based on the extraction of sorbed P by successively stronger reagents, P associated with the sorbent surface may be classified into labile P, partially available and fixed or non-labile fractions (Cross and Schlesinger, 1995). Phosphorus associated with residual or unaccounted fractions (Figures 3.5 and 3.6) must, therefore, be retained through strong mechanisms of retention, presumably ligand exchange and intraparticle P diffusion. The elevated amorphous Al and Fe contents of all the residues (Section 2.3.1) suggests that the exchange between P and H_2O and OH^- on the surfaces and edges of hydrous Fe and Al oxides is a primary means of retention. The relationship between affinity parameters and organically bound Al (Section 3.3.2) does support this contention. Makris *et al.* (2004a, 2004b, and 2005) and Makris and Harris (2006) have noted that the diffusion of P into WTR micropores is a primary means of fixation. The equilibration times used in their studies were, nevertheless, extensive (up to 80 days) and it is likely that the immediate immobilisation of P observed in this study is due to chemisorption processes. While most residues contained elevated quantities of exchangeable Ca, the general absence of P in Ca bound forms and the observed redistribution of Ca-P fractions (Section 3.3.3) suggest that the precipitation of calcium phosphates is of minor importance. The direct relationship between the affinity parameter values and Ca (Section 3.3.2) may simply reflect ligand exchange on calcium carbonates or the sorption of P onto Al and Fe associated with Ca. The redistribution of organically bound P fractions is of particular relevance since it implies that a proportion of P bound to this fraction is mobile. This implies weaker mechanisms of retention, that is, P is adsorbed to organic Al, Fe and Ca components through monodentate ligand exchange, charge neutralisation or proton transfer. Therefore, it is suggested that most of the P added is retained predominantly through ligand exchange, in highly stable residual fractions and partially labile organic pools. It is likely that intraparticle P diffusion and continual sorption processes will, over time, increase residual fractions as P is transferred from labile and partially labile pools into stable mineral forms.

3.3.5 Predicting Residual Phosphorus Concentrations

As noted in Section 3.2.2, the accurate description of sorption data allows for the prediction of quantity-intensity relationships within a given concentration range. A key point, however, is that isotherm parameters are, in theory, only valid for the chemical conditions under which the

experiment was conducted (Goldberg, 2005). In addition to this, factors in the sorbate-sorbent system other than temperature and concentration may affect S/c plots and the term 'isotherm' implies a degree of control which does not exist (Barrow, 1978). Given the heterogeneous nature of the residues and that the procedures were not carried out under ideal conditions of constant temperature and pressure, it is likely that the models failed to accurately predict residual P concentrations (Figure 3.7). However, the similarity of predicted P sorbed values to actual P sorbed values (Appendix 3.10) suggests that the empirical isotherm equations utilised in this study do indeed have predictive capabilities. In the Blackheath residue, for example, the difference between the obtained and predicted P sorbed values for the desorption data was only 3 mg kg⁻¹. These small errors are evidently exacerbated on the x axis of S/c plots where residual concentrations are orders of magnitude less than the quantities of P adsorbed.

The differences between predicted and residual P concentrations for the 7 selected residues are conveniently summarised in Figure 3.7. The implication in cases where obtained values are less than those predicted by the equations (shown as points below the ideal line) (Figures 3.7) is that a greater quantity of P was retained by the residue (e.g. Randwater residue). Conversely, points above this line (e.g. Bloemfontein and Midmar residues) suggest sorption inhibition where less P was adsorbed than predicted by the model. Of interest is the observed linear relationship between actual and predicted concentrations. It is suggested that non-linear (e.g. Bloemfontein residue) points are indicative of residue heterogeneity and are a consequence of variations in particle size or chemical composition between samples. The absence of noticeable outliers (the case for the majority of residues) does, on the other hand, suggest that deviations from predicted values are due to variations in environmental conditions such as temperature and pressure. Temperature, in particular, is known to have a controlling influence on the magnitude of P sorption with the rate of reaction between P and soil surfaces increasing three-fold for every 10 °C rise in temperature (Barrow, 1989). Because experiments were not conducted under ideal isothermal conditions, the apparent discrepancy between observed and predicted values could, therefore, be attributed variations to in laboratory temperature.

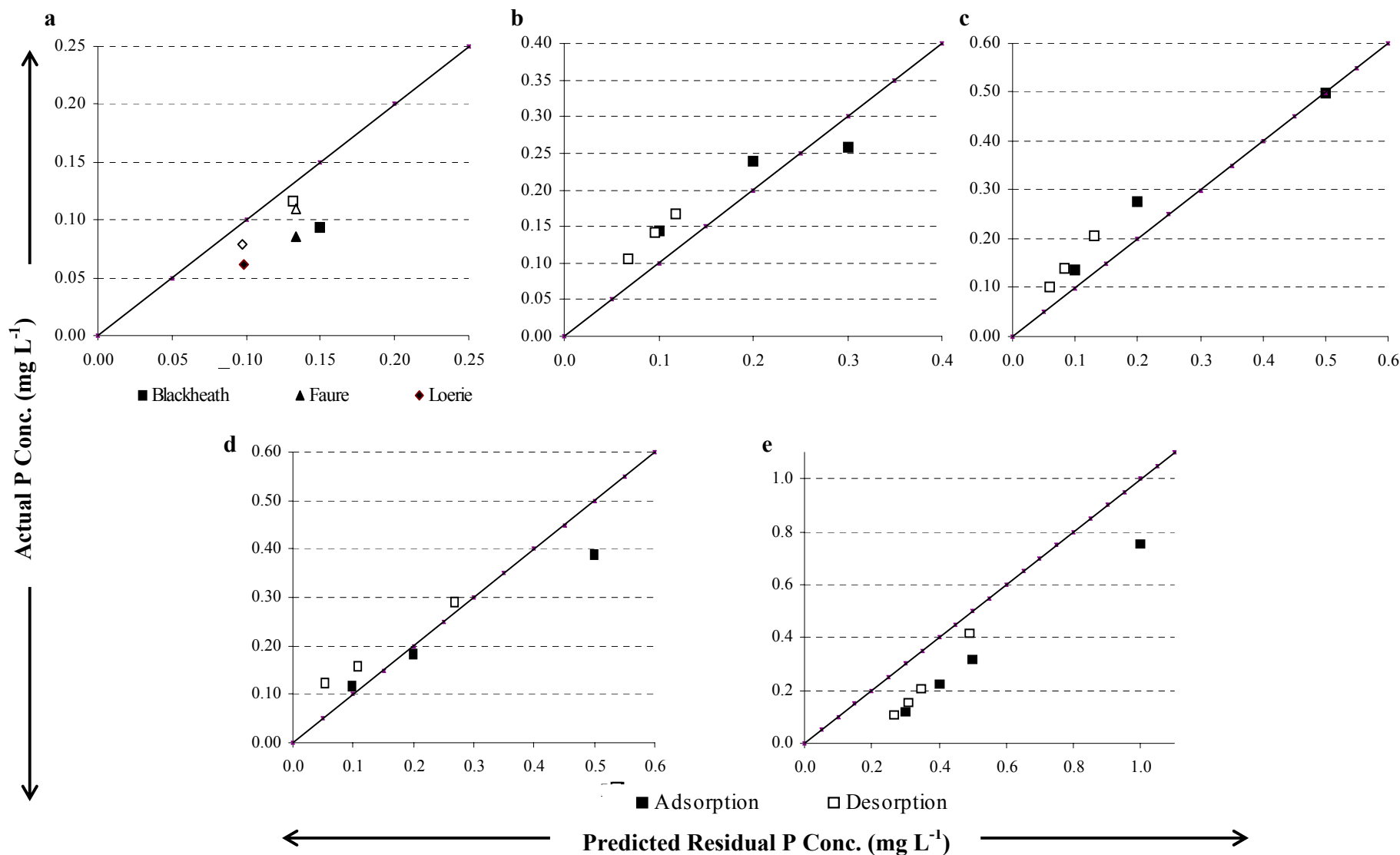


Figure 3.7 Comparison of actual residual P concentrations to concentrations predicted by empirical isotherm equations for the (a) Blackheath, Faure and Loerie, (b) Bloemfontein, (c) Midmar, (d) Nahoon and (e) Randwater WTRs. Adsorption and desorption refer to the data collected during these studies (Sections 3.2.2 and 4.2 respectively). Diagonal line represents an ideal 1:1 relationship.

3.4 General Discussion and Conclusions

The core focus of this study was to gain insight into the processes responsible for the retention of P by 15 South African WTRs. Although mechanisms of retention were, as a result of residue heterogeneity, variable and seemingly complex, a number of processes common to all residues were operative. All residues were shown to be strong sorbents of inorganic P, a feature attributed primarily to their elevated amorphous Al and Fe contents. The fractionation of P treated residues revealed that most of the sorbed P was retained in highly stable residual forms or as a component of organic matter. Phosphorus replenishment capacity is, therefore, restricted even though residual P concentrations were often within adequate ranges for plant growth. The ability of these WTRs to reduce residual P concentrations by fixing P in forms resistant to desorption suggests that they may be used to remediate P polluted soils. Further research is, nevertheless, required to fully assess their effectiveness as environmental amendments since P was only applied at rates relevant to agronomic applications.

Sorption data was described by four empirical adsorption isotherm equations (Langmuir, Freundlich, Temkin and linear) to attempt to elucidate possible mechanisms of P retention. Of the 15 WTRs, 10 were described by the Temkin equation and 2 each by the linear and Freundlich equations. No model was found to fit sorption data derived from the Loerie residue. While all models provided excellent descriptions of the data, the observed positive relationship between the distribution coefficient (K_d) and the quantity of P sorbed (S) indicated that the basic assumptions of the Temkin and Freundlich models were not true for these WTRs. Therefore, the models were used as mathematical descriptors and not for mechanistic interpretation of P sorption behaviour. Given that most of residues were described by the Temkin equation and that K_d had similar patterns of variation does, nonetheless, suggest the operation of P sorption processes common to all residues. Based on the direct relationship between K_d and S, it was suggested that the P induced activation of sorption sites was a process common to all residues. This was corroborated by the fractionation study which showed that P application results in the redistribution of relatively stable organically bound P to highly stable mineral forms. Consequently sorption sites with the highest affinity for P are only occupied once a certain base level of sorption has been achieved.

Phosphorus present in residual forms was thought to be chemisorbed predominantly to hydrous Al and Fe oxides, presumably through ligand exchange. In contrast, the transfer of P from organic fractions suggested that P bound to this component was mobile though not necessarily plant available. A strong positive correlation between model affinity parameters and organically bound Al and Fe confirmed the association of P with this fraction, presumably through monodentate ligand exchange. Although all residues did contain elevated quantities of exchangeable Ca, data from this study suggests that competing adsorption reactions will inhibit the fixation of P through calcium phosphate formation. It was speculated that the direct relationship between affinity parameters and Ca was as a result of ligand exchange on calcium carbonates or the sorption of P onto Al and Fe associated with Ca.

Therefore, the addition of P to WTRs appears to follow a ‘law of diminishing returns’ where less P is desorbed per unit P added as application concentrations increase. This holds true for as long as K_d is an increasing function of S. Thus P application has a net positive impact on residual P contents once high affinity sites are saturated and K_d begins to drop. This threshold is, for most of the residues, only exceeded after P additions (applied as superphosphate) of between 2100 and 4200 kg ha⁻¹. The application of P fertilisers to WTRs to negate P deficiencies is, therefore, highly uneconomical unless sorption sites are already saturated or immobilisation processes inhibited. This study has, however, dealt primarily with the sorption of P onto pure WTRs under laboratory conditions. Under field conditions, sorption processes may be inhibited (Elliott *et al.*, 1990a; Basta, 2000; Hughes *et al.*, 2005) and further research is required to fully elucidate the effects of P application on WTR amended soils.

CHAPTER 4

DESORPTION OF PHOSPHORUS FROM WATER TREATMENT RESIDUES

4.1 Introduction

The ability of water treatment residues (WTRs) to fix labile P fractions has, in an agronomic context, been viewed as detrimental due to the potential for induced plant P deficiencies. Phosphorus immobilisation is, on the other hand, highly desirable in an environmental context where WTRs may be utilised to sorb excess P from surface runoff or aid in the remediation of P polluted soils. Successful application, in either context, depends therefore on the extent to which WTR applications limit bioavailable P pools. Desorption processes are, in this regard, of fundamental importance because they are one of the factors which control soil solution P concentrations (Sato and Comerford, 2006a). Desorption has been defined as the release of a sorbate from a sorbent into the solution phase, without reference to any specific mechanism (Sims and Pierzynski, 2005).

The few studies which have focussed on P desorption from WTRs (Ippolito *et al.*, 2003; Makris *et al.*, 2005) have shown that adsorption processes are effectively irreversible. This has been attributed to strong mechanisms of retention such as ligand exchange (Yang *et al.*, 2006) and the diffusion of P into the interior of particles (Makris *et al.*, 2004a, 2004b, 2005). The noticeable absence of P deficiencies in plants growing under field conditions (Elliott *et al.*, 1990a; Basta, 2000; Hughes *et al.*, 2005) does, however, indicate that a plant's ability to access P on WTR amended soils is not as limited as suggested by many sorption studies. This may be due in part to the so called 'dilution effect' which suggests that the relative quantities of WTR which are typically land applied are negligible with respect to total soil volume and consequently have a minor influence on soil chemistry. The study by Hughes *et al.* (2005) in which ryegrass was found to grow well in pure layers of a polymer WTR does, however, suggest that this is not the case and that WTRs may actually contain sufficient P to support plant growth or that plants are able to release P from the WTR. Phosphorus desorption mechanisms are, in this regard, of particular interest as they provide insight into the processes responsible for the release of P into soil solution.

Mechanistically, the release of inorganic P has been attributed to disequilibria created by removal of P from solution or in response to the action of organic ligands with the sorbent surface (Sato and Comerford, 2006a). Disequilibria desorption and ligand desorption have been categorized further into exchange and dissolution processes (Figure 4.1) (Sato and Comerford, 2006b). In exchange processes, P is desorbed by exchange with anions in solution (disequilibria exchange) or as a result of ligands which form inner-sphere complexes with the sorbent surface (ligand exchange). In dissolution, P is desorbed from relatively soluble compounds (disequilibria dissolution) or by ligands which destabilize and dissolve the sorbent (ligand dissolution).

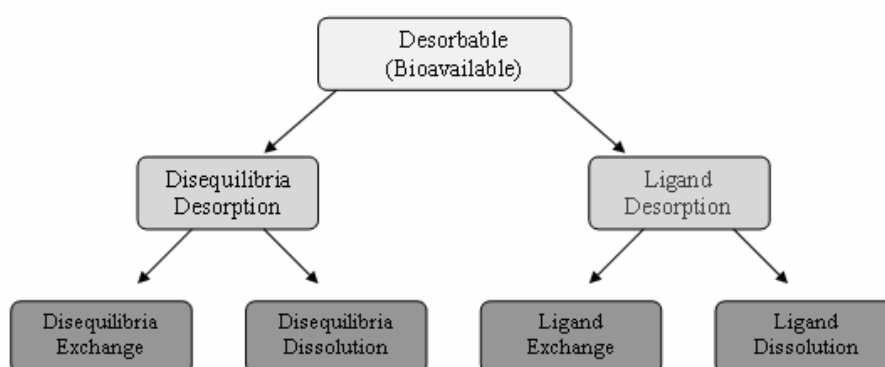


Figure 4.1 Types of inorganic P desorption (adapted from Sato and Comerford, 2006b).

Ligand desorption processes are, in the context of this study, of particular interest given the high affinity of the WTR surface for P. It has been well documented that plants may, through the release of organic ligands with high complexation constants, extract more P than by simple disequilibrium (Nagarajah *et al.*, 1968; Parfitt, 1979; Bhatti *et al.*, 1998). Mobilisation of P has been attributed to the enhanced dissolution of P minerals caused by the acidification and complexation of cations (Ca, Al and Fe) and to the competitive adsorption of P and organic ligands on metal (Geelhoed *et al.*, 1999). The production of organic anions by plant roots, either through exudation (e.g. oxalate, citrate, malate) or respiration (bicarbonate anion), could therefore provide an explanation for the absence of plant P deficiencies on WTR amended soils.

This study has two primary objectives. The first was to investigate the influence of some common soil organic ligands (oxalate, citrate and bicarbonate) on the desorption of P from 15 South African WTRs. A key objective was to contrast disequilibria desorption with ligand desorption processes

and to determine the quantity of P available for release from the untreated WTRs. The second objective was to determine whether desorption was in any way influenced by P application. The extraction of P from P-treated residues tested the hypothesis that the addition of P to WTRs results in an activation of sorption sites thereby adversely affecting P availability.

4.2 Materials and Methods

Fifteen South African WTRs (Table 2.1) were extracted with four different solutions to determine the quantity of P available for desorption from the pure residues. Duplicate samples of 1 g were placed in 50 ml polyethylene centrifuge tubes and shaken for 18 hours with either 25 ml of distilled water or 25 ml of 20 mM bicarbonate (HCO_3^-), oxalate ($\text{C}_2\text{O}_4^{2-}$) or citrate ($\text{C}_6\text{H}_5\text{O}_7^{2-}$) solutions made up from sodium hydrogen carbonate, oxalic acid dihydrate and citric acid monohydrate, respectively. The anion concentrations were based on those commonly found in soil solution (Bhatti *et al.*, 1998; Makris *et al.*, 2005). The oxalate extraction was carried out in the dark to prevent the photo-induced decomposition of oxalate (Loeppert and Inskeep, 1996). Following extraction, samples were centrifuged at 3500 rpm for 10 minutes, filtered through Whatman No. 42 filter paper and analysed for Al, Fe, Ca and P using a Varian (720 ES) inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A Meter Lab PHM 210 standard pH meter was used to record the pHs of all supernatant solutions.

In an effort to gain further insight into potential desorption mechanisms, the above procedure was carried out on WTRs onto which a known quantity of P was sorbed. As in the fractionation experiment (Section 3.2.2), P was sorbed onto seven WTRs (Randwater, Faure, Blackheath, Loerie, Bloemfontein, Midmar and Nahoon) based on their respective predictive models (Section 3.2.2), though in this instance the mass of residue used in the procedure was increased to 1 g. The consequence was that while the applied P concentrations remained the same, the quantity of P sorbed differed, being greater than that of the fractionation experiment (Appendix 3.5). Following sorption, supernatant solutions were centrifuged at 3500 rpm for 10 minutes, filtered through Whatman No. 42 filter paper and analysed for Al, Fe, Ca and P by ICP-AES. Solution pHs were determined with a Meter Lab PHM 210 standard pH meter.

4.3 Results and Discussion

4.3.1 Phosphorus Desorption from Untreated Residues

A low amount of P was extracted during the water extraction for all residues ($< 9 \text{ mg kg}^{-1}$; Table 4.1). Phosphorus extracted in this step, termed disequilibria desorption P, is in equilibrium with P loosely held on the residue surface and is considered as plant available. The water extractable P concentrations are not markedly lower than total labile P values (Table 4.1) (with the exception of the Droogdam WTR) which suggests that long-term P replenishment capacities are limited. Poor P buffer capacities are, therefore, likely to inhibit the ability of WTRs to supply plants with P through disequilibria desorption processes. This is a key point with respect to residual P values (Appendix 4.1) which, for a number of residues, were above the proposed minimum value for plant growth (0.20 mg L^{-1} , Fox and Kamprath, 1970). However, if examined independently, solution P concentrations may give a false impression of P supplying capacity. As noted by Holford (1989), residual values are only useful in combination with a measure of the quantity of P in the solid phase which can pass into the solution during the life of the plant.

The quantity of P released in the presence of bicarbonate, oxalate and citrate was, for all residues, greater than that released by simple disequilibrium reactions (water extraction; Table 4.1). While this confirms that desorption is enhanced by the presence of complexing ligands, P extracted with bicarbonate, oxalate and citrate was, for a number of residues (e.g. Churchill and Voelvrei), still less than total labile P measured by fractionation (Table 4.1). In the case of the bicarbonate extracts this was attributed to the use of a 20 mM solution concentration as opposed to the 1 M solution used in the fractionation study (Section 2.3.2). For the oxalate and citrate extractions, variations in ligand extractable P may be attributed, in part, to P distribution in the WTR. Makris *et al.* (2005) hypothesised that the diffusion of P into WTR micropores restricts the ability of complexing ligands, such as oxalate and citrate, to readily extract P. Therefore low ligand extractable P values (e.g. Randwater and Voelvrei) suggest that most of the P present in the WTR is distributed in regions inaccessible to the action of ligands or is present in highly stable forms which are resistant to ligand exchange or dissolution. The affinity of a ligand for the WTR surface may be viewed as an additional variable in P desorption processes. In the Blackheath residue, for example, the increase in solution P concentration with the addition of citrate (Table 4.1) suggests that the association between this ligand and the sorbent surface is stronger than for oxalate and bicarbonate.

Table 4.1 Quantity of P released (mg kg^{-1}) and residual P concentrations (mg L^{-1}) of 15 South African WTRs after shaking for 18 hours with water (1:25 WTR:water ratio) and 25 ml of 20 mM bicarbonate, oxalate and citrate

WTR	Total Labile P ^a mg kg^{-1}	Water		Bicarbonate		Oxalate		Citrate	
		D	R	D	R	D	R	D	R
Blackheath	18.1	4.05 ± 0.49	0.162 ± 0.02	5.06 ± 1.67	0.202 ± 0.05	12.0 ± 1.9	0.242 ± 0.04	66.7 ± 5.43	2.67 ± 0.65
Bloemfontein	16.2	7.29 ± 2.54	0.292 ± 0.10	14.8 ± 5.0	0.597 ± 0.02	102 ± 17	2.04 ± 0.33	195 ± 8.97	7.80 ± 1.07
Bronkhorstspuit	19.0	2.67 ± 0.59	0.107 ± 0.02	6.15 ± 0.14	0.246 ± 0.05	12.0 ± 2.6	0.242 ± 0.05	15.6 ± 1.05	0.623 ± 0.04
Churchill	9.45	1.61 ± 0.81	0.064 ± 0.03	3.06 ± 0.53	0.123 ± 0.02	9.67 ± 0.85	0.195 ± 0.02	5.14 ± 1.71	0.206 ± 0.04
Droogdam	155	6.74 ± 1.24	0.269 ± 0.05	19.4 ± 5.4	0.775 ± 0.01	116 ± 23	2.34 ± 0.46	366 ± 29.4	14.7 ± 0.12
Elandsjagt	12.8	2.39 ± 0.19	0.095 ± 0.01	3.30 ± 0.22	0.132 ± 0.03	5.83 ± 1.30	0.118 ± 0.03	9.20 ± 1.82	0.368 ± 0.17
Faure	10.0	8.93 ± 1.35	0.357 ± 0.06	9.70 ± 1.07	0.389 ± 0.03	4.41 ± 0.69	0.088 ± 0.01	13.7 ± 2.20	0.548 ± 0.07
Loerie	10.8	1.69 ± 0.57	0.068 ± 0.02	9.74 ± 1.43	0.391 ± 0.09	12.6 ± 3.2	0.252 ± 0.06	78.3 ± 2.80	3.13 ± 0.86
Midmar	12.0	4.19 ± 1.38	0.168 ± 0.06	7.94 ± 1.68	0.317 ± 0.06	18.6 ± 1.1	0.373 ± 0.02	78.6 ± 11.0	3.14 ± 0.30
Nahoon	10.4	8.67 ± 0.26	0.347 ± 0.01	9.54 ± 0.76	0.382 ± 0.09	342 ± 48	0.549 ± 0.08	51.5 ± 11.1	2.06 ± 0.68
Nelspruit	9.38	4.04 ± 0.38	0.162 ± 0.02	3.78 ± 1.70	0.151 ± 0.01	289 ± 31	5.82 ± 0.62	188 ± 2.85	7.54 ± 0.14
Noditgedagt	28.5	6.99 ± 0.68	0.279 ± 0.03	14.5 ± 3.34	0.581 ± 0.14	39.1 ± 2.2	0.785 ± 0.44	666 ± 13.1	26.6 ± 1.80
Randwater	9.38	3.52 ± 1.12	0.141 ± 0.05	6.73 ± 0.71	0.269 ± 0.03	3.38 ± 0.55	0.067 ± 0.01	5.67 ± 0.47	0.227 ± 0.11
Vaalkop	9.20	1.66 ± 0.16	0.066 ± 0.01	3.25 ± 0.77	0.130 ± 0.01	28.8 ± 1.4	0.581 ± 0.03	13.9 ± 3.38	0.555 ± 0.12
Voelvlei	8.99	2.03 ± 0.56	0.081 ± 0.02	3.62 ± 2.09	0.145 ± 0.01	3.25 ± 0.32	0.065 ± 0.01	5.48 ± 0.78	0.219 ± 0.03
Ca(H ₂ PO ₄) ₂ ·H ₂ O ^b		246 000							
Zupancic (1996) ^c		0.05							
Fox and Kamprath (1970) ^d		0.2							

^a Total labile P was calculated as the sum of the inorganic bicarbonate and NaOH fractions (Section 2.3.2).

D P desorbed (mg kg^{-1}). **R** Residual P concentration (mg L^{-1}). ^b mg of P in 1 kg superphosphate.

^{c, d} Proposed minimum residual P concentrations required for plant growth (mg L^{-1}).

Alternatively, P released in the presence of ligands may simply be readsorbed thereby restricting extraction efficiency. Hysteretic action is likely to be encouraged by low phosphorus saturation indices and elevated quantities of reactive Al and Fe oxides (Section 2.3.1). The chemical nature of these processes is, in all likelihood, complicated, variable and influenced numerous factors ranging from solution pH to ligand stereochemistry.

A key objective of this study was to contrast disequilibria desorption with ligand desorption and to determine whether the release of P was due to exchange or dissolution. The dissolution of an associated element, in this case Al, Fe and Ca, was utilised to determine whether the extract was removing ligand-exchangeable or ligand soluble P (Sato and Comerford, 2006b). The changes in solution Al, Fe, Ca and P concentrations relative to the water extract after extraction with bicarbonate, oxalate and citrate are presented in Table 4.2. Negative values indicate the ligand has extracted less of particular element while positive values signify a net release. Therefore values which decrease or remain relatively constant suggest the operation of exchange processes while large increases in solution Al, Fe and Ca are indicative of dissolution. The Bloemfontein residue is a good example of the aforementioned processes (Table 4.2). In both the bicarbonate and oxalate extractions, ligand exchange was the dominant mechanism of P release as shown by Al, Fe and Ca concentrations which either remained constant or declined. In the citrate extraction, however, Al, Fe and Ca concentrations all increased with solution P thereby confirming the operation of a dissolution process.

In most cases, oxalate and citrate resulted in P release through dissolution while P desorbed by bicarbonate was due to exchange. Generally the greatest quantity of P was released through dissolution processes although ligand exchange did result in marked P release from the Bloemfontein and Droogdam residues (Table 4.1). There was, however, no correlation between P release and the dissolution of Al, Fe and Ca (Appendix 4.2). Solution P concentrations remained low for a number of residues (e.g. Faure and Voelvlei) even though the quantities of Al, Fe and Ca released were high (Appendix 4.1). This indicates that the distribution of inherent P is WTR specific and suggests that plant access to ligand extractable pools will vary between WTRs. In certain residues (e.g. Loerie), elevated solution Al and Fe concentrations could be attributed to exchangeable fractions as opposed to the presence of ligand exchange or dissolution mechanisms. Of additional interest was the general absence of correlations between the changes in pH and solution Al, Fe, Ca and P concentrations (Appendix 4.2). This suggests that mineral dissolution was

Table 4.2 Changes in solution pH and the quantities of Al, Fe, Ca and P released after extraction with 20 mM bicarbonate, oxalate and citrate solutions, relative to water extractable Al, Fe, Ca and P (actual values extracted for the P pre-treated residues are presented in Appendix 4.3)

WTR	Bicarbonate					Oxalate					Citrate				
	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH
	Change (mg kg ⁻¹) ^a					Change (mg kg ⁻¹)					Change (mg kg ⁻¹)				
Blackheath	-140	-54.1	-77.5	1.01	1.52	6026	-14.6	313	7.99	-2.90	9927	991	1239	62.7	-4.22
Bloemfontein	0	0	-385	7.51	1.18	0	2.22	-463	94.4	-4.01	409	1364	13037	188	-2.69
Bronkhorstspuit	0	0	-229	3.48	1.42	4211	45.8	326	9.36	-2.50	307	335	1524	12.9	-3.99
Churchill	18.9	7	15.2	1.45	2.46	5788	1703	70.6	8.06	-3.66	623	184	118	3.53	-3.76
Droogdam	0	0	364	12.6	1.15	12.3	4.65	-343	110	-0.55	119	2318	9821	360	-1.20
Elandsjagt	-213	-100	-18.3	0.91	1.67	4872	201	285	3.44	-3.43	2340	402	763	6.82	-4.28
Faure	-128	-674	84.3	0.77	0.91	24.2	1556	-6.22	-4.53	-2.46	352	18067	4064	4.78	-3.27
Loerie	2341	675	-392	8.05	2.74	7021	834	-335	10.9	-2.43	5244	1381	65.7	76.6	-3.12
Midmar	0	0	-349	3.74	1.34	672	753	-533	14.4	-1.42	1570	3392	2949	74.4	-3.54
Nahoon	-779	-398	284	0.87	1.17	1512	3744	50.2	333	-4.93	-199	556	1883	42.8	-4.44
Nelspruit	-659	-521	287	-0.27	1.41	1344	2171	458	285	-4.47	-139	647	1250	184	-4.53
Noditgedagt	-410	-268	91.9	7.53	1.34	-36.0	6747	335	32.1	-3.05	130	10486	2891	659	-4.29
Randwater	-303	-176	-16.1	3.20	1.47	-303	-176	857	-0.14	0.94	-41.7	553	19644	2.14	0.98
Vaalkop	0	0	-159	1.59	0.99	1377	4210	-484	27.1	-5.09	374	1173	1234	12.2	-4.50
Voelvllei	-90.6	-161	103	1.59	1.03	121	1795	-23.7	1.22	-2.29	239	5616	6829	3.45	-3.64

^a Change in solution pHs and elemental concentrations were calculated as the difference between values obtained with the water and ligand extracts.

due mainly to the action of ligands and not as a result of the induced decline in pH. In a study on the role of organic acids on phosphate immobilisation, Johnson and Loeppert (2006) found that there was no evidence for the proton promoted dissolution of ferrihydrite and goethite in the absence of an organic ligand. Similarly, Geelhoed *et al.* (1999) concluded that acidification of the rhizosphere had no significant effect on the availability of adsorbed P to plants. An increase in the availability of sorbed P was attributed primarily to the exudation of low-molecular weight organic anions.

Large decreases in pH will, nevertheless, increase the extent to which dissolution does occur and the elevated solution Al, Fe and Ca concentrations, particularly at low pH values (Appendix 4.1), are in all likelihood a combined function of ligand action and proton induced degradation. It should also be noted that the poor correlation between the variables (Appendix 4.2) also indicates that ligand desorption is a WTR specific process. Mechanisms of desorption and the extent to which P is released are likely to be closely related to chemical properties such as pH, organic matter content and P distribution which have been found to vary between WTRs (Section 2.3.2).

4.3.2 Phosphorus Desorption from Treated Residues

With the exception of the Faure and Loerie residues, P addition resulted in an increase in the quantity of P released by disequilibria desorption (Table 4.3). Although more P was released at higher application rates, the percentage of P desorbed tended to decline with increasing P addition (Appendix 4.4) corroborating the earlier premise (Section 3.2.2) that P sorption sites are activated with addition of P. For example, in the Nahoon, an increase in the quantity of P sorbed (22 to 142 mg kg⁻¹) resulted in a 14 % decrease in percentage of P desorbed. This activation process is greatly enhanced in the Faure and Loerie residues where P desorbed from the untreated WTRs was greater than that released from the treated WTRs. Phosphorus application appeared to have a negative effect on P desorption by bicarbonate, oxalate and citrate. For example, in the Randwater residue, the quantity of P desorbed by disequilibria (water extraction) was generally greater than that desorbed in the presence of a ligand. Even in cases where a treated WTR released more P than the untreated WTR (e.g. citrate extraction for the Blackheath residue) (Table 4.3), the net quantity of P released was still much less than the quantity of P sorbed by the WTR. Inhibited desorption may be attributed to the combined effects of ligand deactivation and P immobilisation. Phosphorus application may, through exchange processes, release sorbed components into solution thereby reducing ligand activity through complexation or precipitation.

Table 4.3 Quantity of P desorbed from 7 WTRs pre-treated with P in accordance with respective empirical adsorption isotherm equations (Section 3.2.2)

WTR	P sorbed by WTR (mg kg ⁻¹)	P Desorbed (mg kg ⁻¹)							
		Water		Bicarbonate		Oxalate		Citrate	
		T	U	T	U	T	U	T	U
Blackheath	152	12.3	4.05	1.96	5.06	16.1	12.0	85.9	66.7
Faure	132	8.41	8.93	9.51	9.70	3.14	4.41	10.2	13.7
Bloemfontein	71.6	17.9		22.1		5.87		168	
	141	32.0	7.29	26.4	14.8	7.79	102	205	195
	183	37.7		26.8		9.43		219	
Midmar	151	9.92		12.9		14.6		48.3	
	251	18.6	4.19	19.6	7.94	18.6	18.6	56.9	78.6
	386	28.6		25.9		29.0		104	
Randwater	57.2	20.2		6.79		0.93		11.0	
	123	17.1	3.52	20.2	6.73	1.17	3.38	14.7	5.67
	177	26.3		18.5		2.74		24.6	
	341	65.0		34.7		17.6		34.4	
Nahoon	21.9	9.80		4.87		104		25.1	
	50.7	14.2	8.67	9.70	9.54	116	342	30.5	51.5
	142	27.6		14.4		139		51.6	
Loerie	200	0.93	1.69	12.2	9.74	25.4	12.6	76.3	78.3

T P desorbed from P-treated residue. U P desorbed from untreated residue.

The tendency for oxalate to precipitate with Ca (Loeppert and Inskeep, 1996) suggests that restricted desorption in the oxalate extracts was due to the precipitation of Ca-oxalate salts. Ligand deactivation or degradation is also encouraged by competing adsorption reactions. Geelhoed *et al.* (1999) examined the effect of citrate ligand degradation at high and low amounts of applied P to goethite. They found that, 84 % and 58 %, of applied citrate was degraded at the high and low P applications, respectively. Geelhoed *et al.* (1999) suggested that the adsorbed citrate was protected from degradation and more effective at releasing sorbed P. In this study, the observation that declines in extracted P were generally accompanied by a marked decline in dissolution (Appendix 4.5), suggests that ligand degradation is encouraged by competition for sorption sites. The observed decline in desorption with P application also suggests that applied P is strongly sorbed or retained in areas which are inaccessible or protected from the action of organic ligands. This is in agreement

with Makris *et al.* (2004a, 2004b, and 2005) and Makris and Harris (2006) who found that the fixation or absorption of P is due largely to intraparticle diffusion of P into WTR micropores. Thus P application may inhibit ligand desorption, presumably through the activation of sorption sites and subsequent redistribution of applied and inherent P fractions. The diffusion of P into WTR is, however, a slow process associated with the secondary phase of absorption. Because of the short equilibration times used in this study (18 hours) inhibited desorption was probably a result of ligand deactivation. Figures 4.2 and 4.3 relate the change in solution Al (∂ Al), Fe (∂ Fe), Ca (∂ Ca) and P (∂ P) concentrations (with respect to the water extract) to the amount of P adsorbed for those residues with more than one P application concentration (Bloemfontein, Midmar, Randwater and Nahoon). Data for the Blackheath, Faure and Loerie residues are presented in Appendix 4.5. Although mechanisms of P release appear to be complex and highly variable, a number of general trends are present which aid in the interpretation of this data.

Ligand extractable P was found to be inversely related to the quantity of P adsorbed. For the bicarbonate and oxalate extracts, ∂ Al + ∂ Fe and ∂ P declined with the quantity of P adsorbed while ∂ Ca tended to increase or remain relatively constant (Figures 4.2 and 4.3). Given that most of the ∂ Al + ∂ Fe and ∂ P values were negative indicates that more Al, Fe and P was released in the water extract. Phosphorus desorbed in the presence of bicarbonate and oxalate was, therefore, not due to ligand dissolution but rather a loosely held P component released into solution by disequilibria dissolution. For the citrate extracts, ∂ Al + ∂ Fe and ∂ Ca tended to decrease before increasing or remaining constant (Figures 4.2 and 4.3) at higher P applications. The extent of dissolution and P release was, in general, greater than for oxalate and bicarbonate, perhaps reflecting the observation by Parfitt (1979) that desorption increases with the number of carboxylate groups on the organic ligand. The Nahoon residue was a notable exception and, as with desorption from the untreated residue, (Section 4.3.1), oxalate extracted the greatest quantity of P. Ligand dissolution was, therefore, operative to a greater extent in the citrate extraction although the magnitude of P release, was for all residues, still a small fraction of the quantity of P adsorbed.

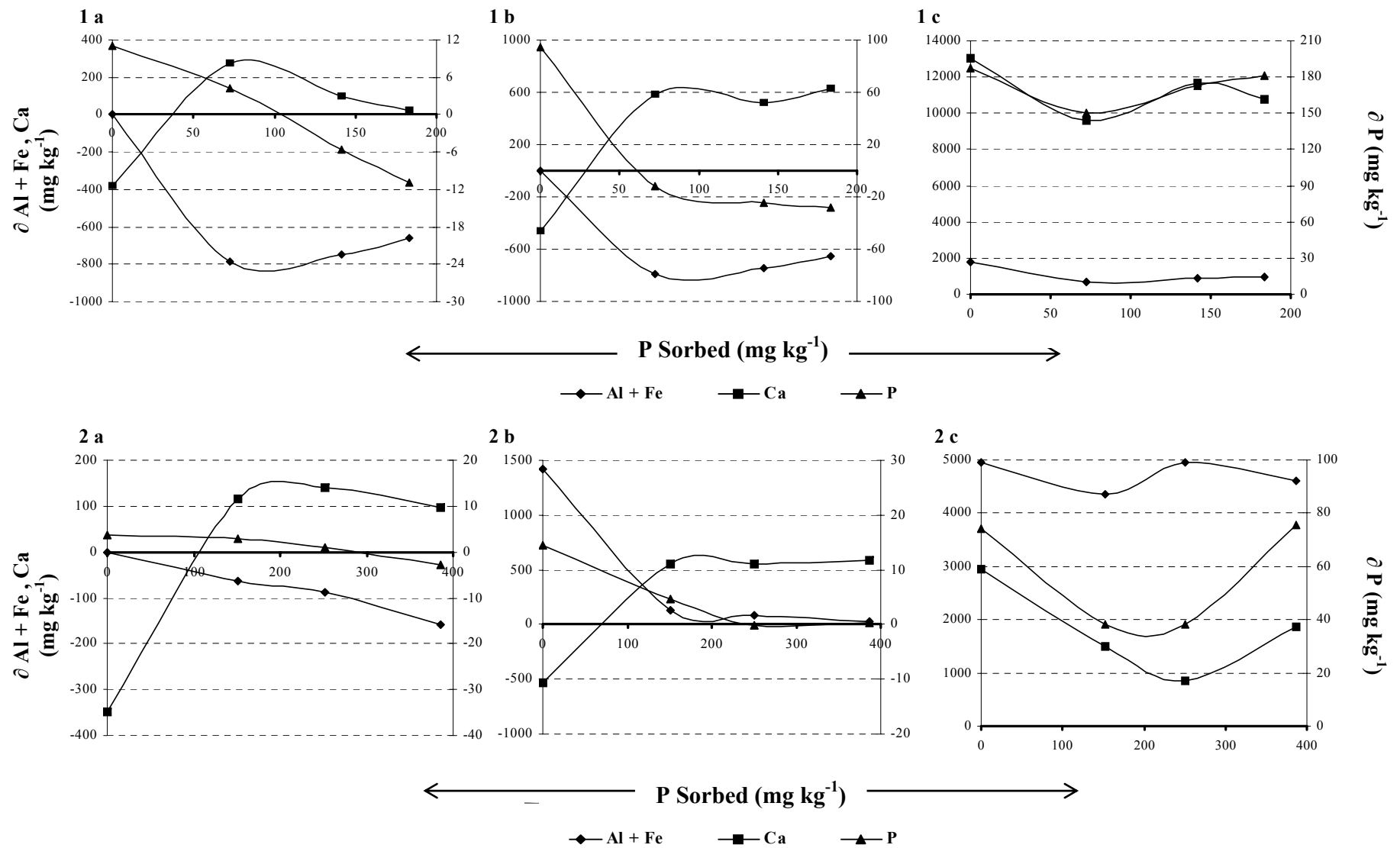


Figure 4.2 Change in solution Al + Fe, Ca and P concentrations with P sorbed for (1) Bloemfontein and (2) Midmar WTRs after extraction with 20 mM (a) bicarbonate, (b) oxalate and (c) citrate.

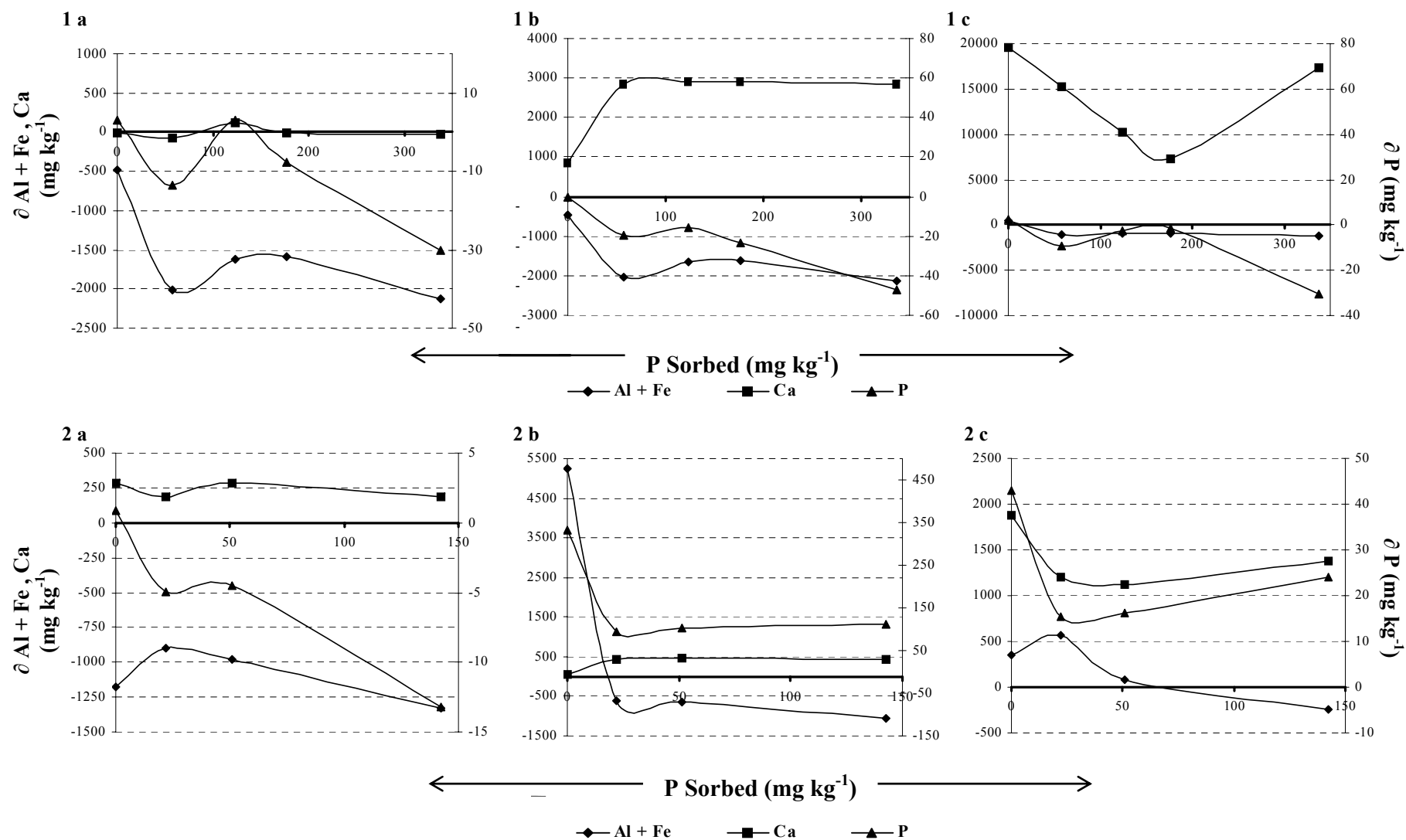


Figure 4.3 Change in solution Al + Fe, Ca and P concentrations with P sorbed for (1) Randwater and (2) Nahoon WTRs after extraction with 20 mM (a) bicarbonate, (b) oxalate and (c) citrate.

As in Section 4.3.1, no clear correlations were found between the respective variables (data not shown) except for a negative correlation (-0.80) between $\partial \text{Al} + \text{Fe}$ and ∂pH for the oxalate extract. As before the lack of correlation between the variables supports the notion that there is specificity in WTR-P desorption processes. The correlation between $\partial \text{Al} + \text{Fe}$ and ∂pH for the oxalate extraction (Figure 4.4) indicates that mineral dissolution was enhanced by a decline in pH (except for the Nahoon residue). The net changes in solution Al and Fe contents were, however, mostly negative and it is unlikely that proton induced dissolution had a major impact on P release. This idea is confirmed by the relationship between ∂P and ∂pH (Figure 4.5). Although a strong negative correlation exists between the two variables, a significant quantity of P is only released through dissolution when ∂pH is large (Figure 4.5). Phosphorus release is, therefore, due primarily to the action of ligands except in poorly buffered residues (e.g. Nahoon) where acidic extractions result in an excessive decline in pH.

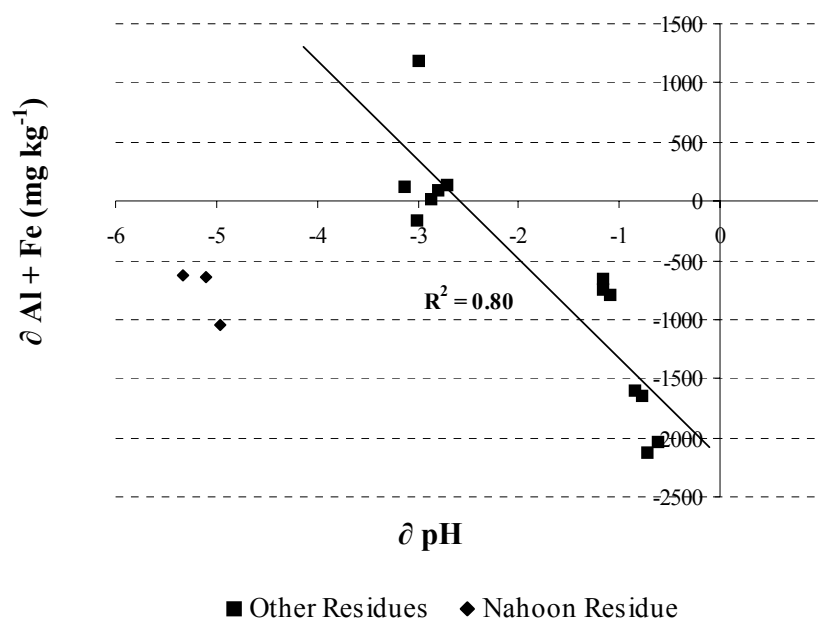


Figure 4.4 Relationship between the change in solution Al and Fe ($\partial \text{Al} + \partial \text{Fe}$) contents and the change in solution pHs (∂pH) (calculated relative to the water extract) for 7 WTRs pre-treated with P and extracted with 20 mM oxalate.

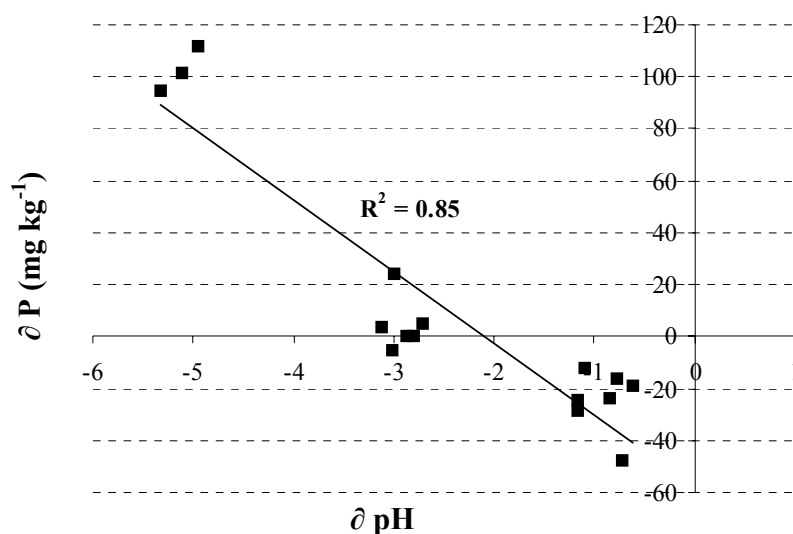


Figure 4.5 Relationship between the change in solution P (ΔP) contents and the change in solution pH (ΔpH) (calculated relative to the water extract) for 7 WTRs pre-treated with P and extracted with 20 mM oxalate.

4.3.3 Phosphorus Adsorption Processes

While the focus of this chapter is on P desorption from WTRs, data from this study does provide additional insight into mechanisms of adsorption. Data from the water extract (Appendix 4.3) is of particular interest as pH variations and solution concentrations of Al, Fe and Ca may be compared directly to the quantity of P adsorbed. With the exception of the Nahoon residue, solution pH increased with P addition suggesting that P was sorbed through an exchange with OH^- on the surface of Al and Fe oxides (Section 1.3.2). In the Nahoon residue a decline in pH may simply reflect a limited buffer capacity and not necessarily the absence of a ligand exchange mechanism. Alternatively, an observed decrease may indicate a mechanism of adsorption involving proton transfer (Section 1.3.2). The dissociation of applied orthophosphate may also mask the hydroxyl induced rise in pH due to ligand exchange. pH data (Appendix 3.2) does not, therefore, provide conclusive evidence of a particular sorption mechanism or the absence of another because variations are dependent on a range of treatment and sorbent variables. An increase in solution pH does, nevertheless, strongly suggest the operation of ligand exchange because no other mechanism results in the release of OH^- .

Solution Al and Fe contents varied in accordance with the fitted models. Phosphorus application resulted in an increase in solution Al and Fe for those residues described by the Temkin isotherm (Bloemfontein, Midmar and Randwater) while the quantity of Al and Fe released declined or remained constant for those residues described by the Freundlich (Nahoon) and linear (Blackheath and Faure) models (Appendix 4.4). In the Bloemfontein, Midmar and Randwater residues, a strong positive correlation between Al + Fe and pH ($R^2 = 0.89$) (data not shown) indicates that this increase was due to dissolution. The hydroxyl induced release of Al and Fe may explain why distribution coefficients (K_d) increased with P application (Section 3.2.2). At low application rates, the acidity from the dissociation of orthophosphate is insufficient to neutralise OH^- released by ligand exchange. The subsequent increase in pH enhances mineral dissolution which results in the exposure of new adsorption sites and K_d increases (Section 3.2.2). As the orthophosphate concentration increases, a greater proportion of OH^- is neutralised, dissolution is restricted and K_d then decreases. Thus the direct relationship between K_d and pH, observed for Bloemfontein, Droogdam, Midmar, Noditgedagt and Voelvlei residues (Appendix 4.6), suggests that the activation of sorption sites may be attributed to mineral dissolution. Poor correlation coefficients, on the other hand, imply that sorption site activation is a function of additional variables or occurs through an alternative mechanism such as the one outlined in Section 3.2.3.

The quantity of Ca released in the water extract decreased markedly with P application for all residues. This suggests that P is either binding with Ca resulting in its immobilisation or that soluble P is becoming less exchangeable due to the activation of sorption sites. Evidence from the ligand extractions suggests that the former process is operative, that is, solution Ca concentrations are reduced in the presence of P due to the precipitation of insoluble Ca-P mineral phases. Although no correlation exists between Ca and P in the oxalate and citrate extractions (data not shown), it is evident that an increase or decrease in Ca dissolution was, in most cases, accompanied by a respective increase or decrease in the quantity of P released (Appendix 4.3). Thus the association between P and Ca appears to be of greater significance than previously suggested (Section 3.2.3). However, changes in P released were seldom large even though ∂ Ca values often were (Appendix 4.5) and it seems likely that the majority of applied P is still retained on the surfaces of hydrous iron and aluminium oxides.

4.4 General Discussion and Conclusions

A greater quantity of P was released from 15 South African WTRs in the presence of bicarbonate, oxalate and citrate than in water thus confirming the hypothesis that plants can, through the exudation of organic anions, extract more P than through simple disequilibria. The magnitude of release did, however, vary greatly and ligand induced desorption was, for a number of residues, no greater than total labile P contents. The majority of inherent P was, in such cases, said to be present in mineral forms with high P complexation constants (Bhatti *et al.*, 1998) or distributed in regions inaccessible to the action of ligands (Makris *et al.*, 2005). Therefore, the ability of plants to access P through both disequilibria and ligand desorption is, for at least half of the residues (Bronkhorstspuit, Churchill, Elandsjagt, Faure, Randwater, Vaalkop and Voelvlei), seemingly restricted. However residual P concentrations were, for a number of residues, greater than the minimum value required for plant growth suggested by Fox and Kamprath (1970; 0.20 mg L^{-1}) which suggests that many residues have the capacity to supply plants with at least a temporary source of P. Phosphorus replenishment capacities are, however, likely to be severely limited by the absence of P in readily available and ligand exchangeable forms. In contrast, the marked increase in ligand extractable P for the Blackheath, Bloemfontein, Droogdam, Loerie, Midmar, Nahoon, Nelspruit and Noditgedagt WTRs suggests that these residues have a greater capacity to maintain residual P concentrations at the levels required for plant growth. Therefore, while quantities of P available for desorption are still considerably less than commercial sources of P (e.g. superphosphate), land application of certain WTRs may increase bioavailable pools of P. This observation may explain, at least in part, why plant P deficiencies are absent under the field application of WTRs.

The release of P occurred primarily through dissolution in the presence of oxalate and citrate and through exchange in the presence of bicarbonate. The greatest quantity of P was always released through dissolution which suggests that the majority of inherent P is present in resistant, non-exchangeable forms. This premise was confirmed by the water extract in which the quantity of P desorbed from all of the residues by simple disequilibrium was minimal ($< 9 \text{ mg kg}^{-1}$). The stability of this inherent fraction is of benefit in the context of environmental applications, particularly in soils with poor P sorbing capacities. Although solution Al and Fe concentrations were elevated and of potential concern, dissolution was only enhanced at very low pH values. Contamination by Al

and Fe is, therefore, likely to be of concern only in very acid soils where the residual alkalinity of a WTR is rapidly neutralised.

The application of P to seven selected residues resulted in a general increase in the quantity of P desorbed by disequilibria (water extraction) and exchange with bicarbonate. A key observation, however, was that percentage P desorbed tended to decrease with increasing P application. The observed decline in extraction efficiency was exacerbated in the presence of oxalate and citrate where the quantity of P desorbed from the untreated residues, was for a number of cases, greater than quantity of P desorbed from the treated samples. Inhibited desorption was for all residues, attributed to an increase in the affinity of the WTR surface for P, thus corroborating the hypothesis that P addition activates sorption sites thereby reducing the efficiency of P applications. The majority of this P appears to be strongly chemisorbed to Al and Fe oxides through hydroxyl ligand exchange although the observed decline in water soluble Ca with P addition suggests an association between these two elements. Oxalate and citrate induced desorption appeared to be further inhibited by a competitive adsorption effect which enhanced ligand degradation. The application of P to WTRs within agronomic ranges is therefore, in light of these findings, a counterproductive process. This is, as noted by Ippolito *et al.* (2003), in direct opposition to the suggestion of Butkus *et al.*, (1998) of adding P to WTRs as a pre-treatment to convert them from P consumers to P suppliers. Long-term immobilisation processes associated with the secondary phase of absorption (e.g. intraparticle P diffusion) are likely to further restrict P release processes. Applying P to WTRs to correct P deficiencies is, therefore, an uneconomical process unless sorption sites are already saturated and immobilisation processes are inhibited.

CHAPTER 5

GENERAL DISCUSSION AND CONCLUSIONS

5.1 Agricultural Implications for Land Application

The 15 South African water treatment residues (WTRs) utilised in this study varied considerably in chemical composition (Chapter 2). However, all residues were found to be effective at retaining phosphorus (P), a characteristic attributed to their elevated Ca and amorphous Al and Fe contents (Chapter 3). Most of the added P was fixed in highly stable forms, through ligand exchange and precipitation with Ca and was resistant to both disequilibria and ligand desorption processes (Chapter 4). These findings are in agreement with numerous laboratory based studies (Chapter 1) which have suggested that WTRs may have a detrimental effect on soil labile P thereby restricting their use as agricultural amendments. This argument contradicts the findings of field based studies which have shown that the land application of these residues has no detrimental effects on plant P uptake. Therefore, a core focus of this study was to quantify labile pools of P in the both raw and P treated residues and to determine possible reasons for the discrepancy between laboratory data and field based observations.

As noted in Section 1.6, the absence of plant P deficiencies has to be attributed to one or more of the following processes:

1. plant P deficiencies are absent because WTRs have little effect on soil P chemistry due to a dilution effect;
2. sorption of P onto WTRs in the field is restricted or inhibited; and
3. that plants growing in the field have the ability or mechanisms to extract sufficient P from the residues.

Therefore the land application of WTRs either increases plant available fractions (3) or has no net effect on plant P nutrition (1 and 2). The fractionation of P in the untreated residues (Section 2) revealed that most of the inherent P was present in forms resistant to desorption through simple disequilibria processes. So while residual P concentrations were often within ranges adequate for plant growth (0.20 mg P L^{-1} ; Fox and Kamprath, 1970), poor P buffer capacities suggested that the immediate contribution of WTRs to soil labile P would be limited and probably negligible. Data

from the desorption study did indicate that bio-available P pools could be increased markedly through the action of organic ligands, a possible mechanism for plants to mobilise fixed P (3). A key point, however, is that P released through both disequilibria and ligand desorption was insufficient to offset the high P sorption capacities. The retention of P by WTRs under field conditions must, therefore, be restricted or inhibited to the extent that the net quantities of P released are equal to or greater than the quantities of P retained (2).

Both the adsorption and desorption studies showed that the application of P to WTRs, within agronomic ranges, enhances P sorption processes. The affinity of the WTR surface for P was found to be the highest at P applications of between 16 and 32 mg L⁻¹, a characteristic attributed to the activation of sorption sites. This provides a plausible explanation for restricted sorption under field conditions where solution P concentrations rarely exceed 0.3 mg L⁻¹ (Fried and Shappiro, 1961). The absence of plant P deficiencies may, therefore, be attributed to the absence of activation, that is, soil solution P concentrations are sufficiently low to prevent the activation of sites with the highest affinity for P. Conversely, in situations where solution P concentrations are elevated, as is often the case with pot experiments, sorption site activation results in the fixation of greater quantities of labile P. Nutrient deficiencies may be exacerbated further in pot experiments due to enhanced microbial activity (higher glasshouse temperatures and favourable moisture regimes), nutrient imbalances and unrealistic plant populations (Hughes *et al.*, 2005).

A number of additional processes are expected to contribute to sorption inhibition. Berkowitz *et al.* (2006) found that the transformation of amorphous aluminium hydroxide to gibbsite in an alum floc resulted in surface area reductions over time thereby decreasing P sorption capacities. As one of the principal sorbents of inorganic P in WTRs, the transformation of amorphous Al and Fe oxides to less reactive forms will greatly inhibit the fixation of labile P in WTR amended soils. Phosphorus sorption is likely to be further restricted by competitive adsorption effects. In a study by Bhatti *et al.* (1998), P sorption to a spodic horizon was decreased by as much as 30 % in the presence of soil organic matter and oxalate. Organic matter and complexing ligands (released by microbes and plants) may, therefore, occupy or mask WTR sorption sites thereby restricting P retention. Therefore, it is suggested that the absence of plant P deficiencies under the field application of WTRs is primarily the result of inhibited adsorption. The immediate immobilisation of P is prevented by the low solution P concentrations of typical soils while P fixation is, over time, further restricted by aging effects and competitive adsorption. Furthermore, low labile P contents and poor

P buffer capacities indicate that the majority of residues will not make a significant contribution to labile P fractions in soil. This, in conjunction with their physical stability (Hughes *et al.*, 2005) and chemically benign nature, suggests that WTRs will have a minimal impact on the P chemistry of unfertilised soils. In an agronomic context, however, P application is routinely a prerequisite to productivity. Data from this study suggests that the efficiency of P fertiliser applications to WTR amended soils may be reduced by P induced activation of sorption sites. This has broad economic implications and further research is required to determine the effects of P application on WTR amended soils.

5.2 Environmental Implications of Land Application

The results of this study suggest that the land application of 15 South African WTRs will have a minimal impact on the environment. Data from the desorption study suggested that most of the South African WTRs will not induce eutrophication through the leaching of labile P. In most cases, the quantities of P desorbed by disequilibria were too small to warrant concern. Even in cases where P release was elevated, total labile pools of P were limited. Moreover, P desorbed during a water extract represents a worst case scenario where disequilibria desorption is maximised. Phosphorus which is desorbed in a natural system will most likely be readsorbed by soil surfaces or be assimilated by microorganisms before being transferred to an aquifer. Phosphorus pollution is, however, due largely to the particulate transport of P and further research is required to determine the effects of WTR amendments on the sediment transport of P-rich particles.

Of concern is the potential impact of WTR amendments on soil solution Al and Fe contents. The observed inverse relationship between solution Al and Fe and pH suggest that the concentration of these elements in soil solution may be increased when WTRs are applied to acid soils. The magnitude of release does, however, vary substantially which suggests that the environmental and agricultural problems associated with Al and Fe toxicity may be avoided by simply applying residues with high Al and Fe contents to neutral or slightly alkaline soils.

The utilisation of P concentrations relevant to agricultural application (0 to 128 mg P L⁻¹) meant that P sorption maxima were not achieved. The vast majority of applied P was, nevertheless, fixed in highly stable mineral forms resistant to desorption. This confirms the notion that WTRs may be used

as eutrophication preventatives although chemical heterogeneity suggests that P sorption capacities are likely to vary significantly. It is, therefore, imperative that a particular WTR be thoroughly characterised prior to its use as an environmental amendment to ensure that the desired results are achieved.

5.3 Further Research

The vast majority of research regarding the land application of WTRs has been based on quantifying P sorption processes under carefully controlled laboratory conditions. There is a definite lack of research into the field application of these residues under varying environmental conditions. Therefore, the extent and consequences of in field WTR-P sorption processes have not been fully assessed, even though field based studies suggest the land application of WTRs to be of minimal impact. It is suggested that future research be directed primarily at field experimentation based on the outcomes of the numerous laboratory and pot experiments already conducted. A key objective would be to determine the immediate and long term impacts that a range of residues, of varying chemical compositions, have on bioavailable pools of P. The chemical heterogeneity of WTRs certainly suggests that their impacts on soil P chemistry will more varied than suggested by current field studies.

Further research is, in particular, required to confirm whether the direct relationship between K_d and S is due to the P induced activation of sorption sites. Field trials and pot experiments involving the application of variable quantities of P fertiliser to WTR amended soils may indicate whether this process is of any practical relevance. Additional studies are also required to fully elucidate mechanisms of retention which are, as demonstrated by this study, complex and variable. The use of analytical techniques such as x-ray diffraction (XRD) and electron microprobe–wavelength dispersive spectroscopy (EMPA-WDS) and equilibrium speciation models (e.g. MINTEQ) would aid in the mechanistic interpretation of sorption data. Of additional interest are the mechanisms and processes which might restrict P sorption processes. Sorption inhibition is of particular relevance in an environmental context where WTRs are used as eutrophication preventatives. Future research into aging effects and competitive adsorption may also serve to clarify the discrepancy between laboratory data and field based observation.

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Appendix 2.1 Chemical characteristics of 15 South African water treatment residues (Herselman, 2009)

WTR	Cd ^a	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Ca ^b	Mg	Na	K	CEC	Total Bases
	mg kg ⁻¹									cmol _c kg ⁻¹					
Blackheath	0.11	0.00	0.30	0.00	0.91	37.30	0.00	0.00	0.00	8.05	1.27	1.09	0.16	6.71	10.57
Bloemfontein	0.10	0.00	0.82	0.21	0.35	2.76	0.00	0.00	0.00	18.87	14.20	1.47	0.00	29.99	34.53
Bronkhorstspuit	0.09	0.24	0.17	0.78	30.60	7.15	1.24	0.20	0.12	15.37	4.78	0.91	0.32	23.41	21.38
Churchill	0.08	0.00	0.36	0.00	0.85	10.51	0.00	0.00	0.00	1.19	1.16	1.01	0.09	1.37	3.44
Droogdam	0.18	0.00	0.25	0.08	0.52	1.38	0.10	0.00	0.00	44.81	14.81	1.22	1.02	51.52	61.86
Elandsjagt	0.11	0.00	0.31	0.00	0.71	4.63	0.00	0.00	0.00	5.39	2.82	1.49	0.27	7.99	9.97
Faure	0.14	0.00	0.28	0.00	0.18	40.38	0.00	0.00	0.00	27.83	24.11	1.20	0.15	39.95	53.28
Loerie	0.11	0.00	0.32	0.00	7.39	42.58	0.00	0.00	0.00	2.87	1.22	1.39	0.28	4.27	5.77
Midmar	0.09	0.00	0.49	0.13	0.82	5.66	0.00	0.00	0.00	19.26	8.21	1.13	0.40	23.52	28.99
Nahoon	0.08	0.00	0.51	0.00	0.47	0.61	0.00	0.00	0.00	13.77	6.55	1.64	0.56	18.51	22.52
Nelspruit	0.09	0.00	0.42	0.00	0.28	4.68	0.00	0.00	0.00	11.91	6.38	0.83	0.14	13.06	19.26
Noditgedagt	0.12	0.00	0.41	0.00	0.35	9.95	0.00	0.00	0.00	18.42	10.61	2.90	0.86	26.12	32.80
Randwater	0.11	0.00	0.13	0.06	0.10	0.19	0.00	0.53	0.12	6.54	19.87	0.68	0.55	19.27	27.65
Vaalkop	0.15	0.00	0.24	0.00	0.21	4.35	0.04	0.00	0.00	17.13	5.50	1.04	0.41	18.82	24.08
Voelvlei	0.14	0.00	0.26	0.00	0.22	0.59	0.00	0.00	0.00	18.70	5.90	1.01	0.26	22.56	25.87

^a Selected heavy metals were extracted with 1 M ammonium nitrate (NH₄NO₃).

^b Exchangeable Ca, Mg, Na and K extracted with 0.1 M strontium chloride (SrCl₂).

Appendix 2.2 Outline of the fractionation procedure used to determined the distribution of P within 15 South African water treatment residues (adapted from Zhang and Mackenzie, 1997)

Extractant	P Fraction	Procedure
None	P bound to the WTR	0.5 g WTR shaken with 0, 2, 4, 8, 16, 32, 64 and 128 mg P L ⁻¹ for 18 hours
30 ml 1 M NaHCO ₃	Soluble and loosely held P _i and P _o	Shake for 16 hours, centrifuge at 4000 rpm for 10 min and pass through Whatman No. 42 filter paper
30 ml 0.1 M NaOH	Aluminium and iron oxide surface bound P _i and P _o	Shake for 16 h and centrifuge at 4000 rpm for 10 min
30 ml 1 M HCl	Calcium bound P _i	Shake for 16 h and centrifuge at 4000 rpm for 10 min
H ₂ SO ₄ – H ₂ O ₂ digestion	Residual P	Add 5ml Conc. H ₂ SO ₄ and 5ml H ₂ O ₂ and digest at 360 °C for 3 hrs

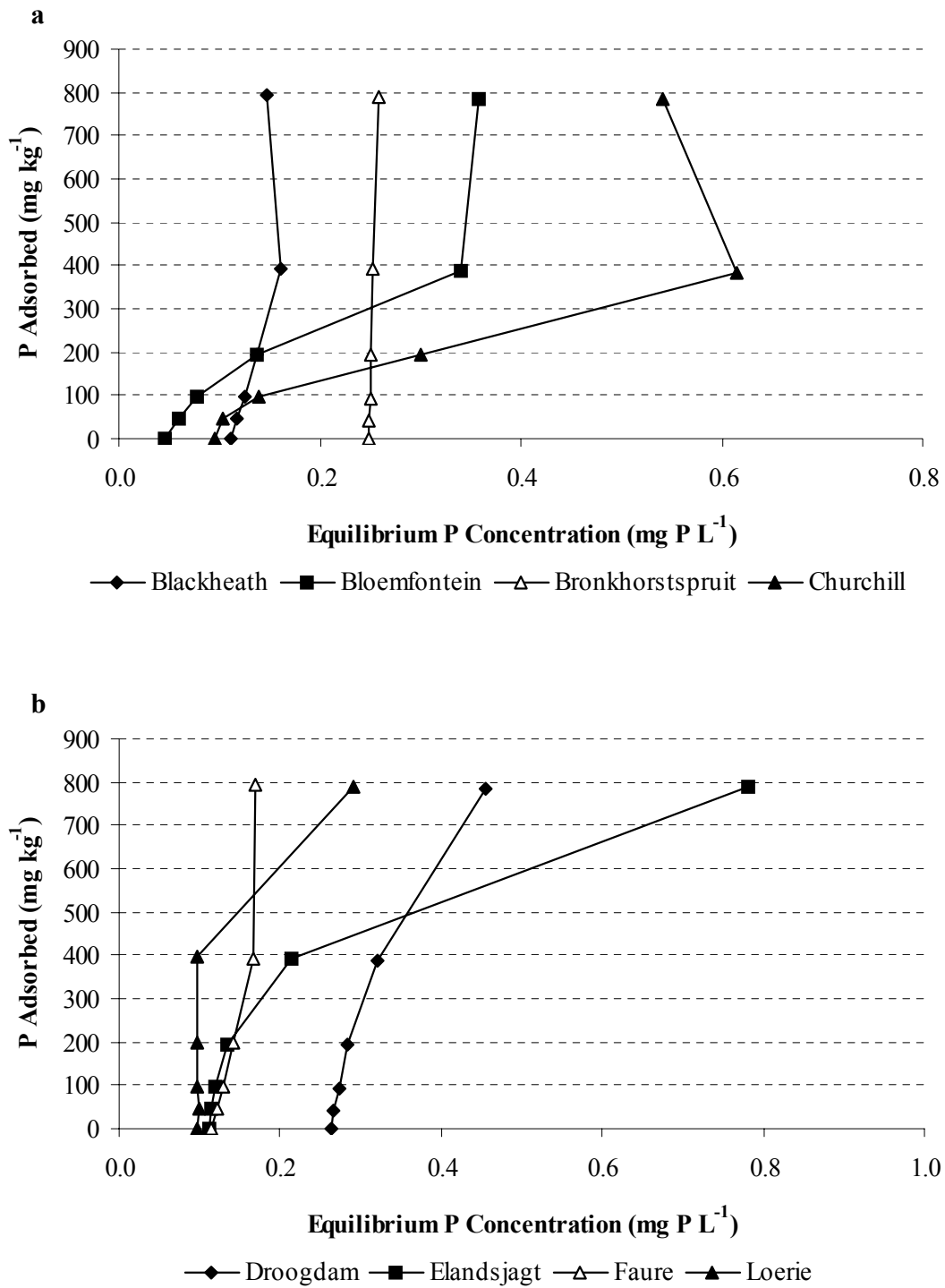
Appendix 2.3 Correlation table detailing the relations between WTR chemical properties and P fractions

	pH	Ca	Dith ^a Al	Dith Fe	Ox ^b Al	Ox Fe	Pyr ^c Al	Pyr Fe	OC ^d	Bicarb Pi	NaOH Pi	Po ^d	HCl Pi
Ca	0.38												
Dithi Al	-0.04	-0.23											
Dithi Fe	0.13	0.50	-0.09										
Ox Al	-0.47	-0.17	0.53	0.01									
Ox Fe	0.15	0.65	-0.13	0.96	0.00								
Pyr Al	-0.55	-0.49	0.68	-0.04	0.88	-0.13							
Pyr Fe	0.01	0.31	0.03	0.89	0.02	0.84	0.08						
OC	-0.37	-0.30	0.78	-0.04	0.56	-0.05	0.67	0.06					
Bicarb Pi	0.08	0.73	-0.26	0.01	0.04	0.24	-0.31	-0.11	-0.22				
NaOH Pi	0.01	0.74	-0.05	0.12	0.23	0.34	-0.12	-0.04	0.00	0.86			
Po	-0.14	-0.53	-0.05	-0.17	-0.15	-0.31	0.13	0.09	-0.11	-0.44	-0.70		
HCl Pi	0.07	0.76	-0.17	0.10	0.12	0.33	-0.24	-0.05	-0.13	0.88	0.98	-0.65	
P Resid.	0.15	0.02	0.18	0.14	0.06	0.12	0.01	-0.08	0.22	-0.22	0.04	-0.74	-0.02

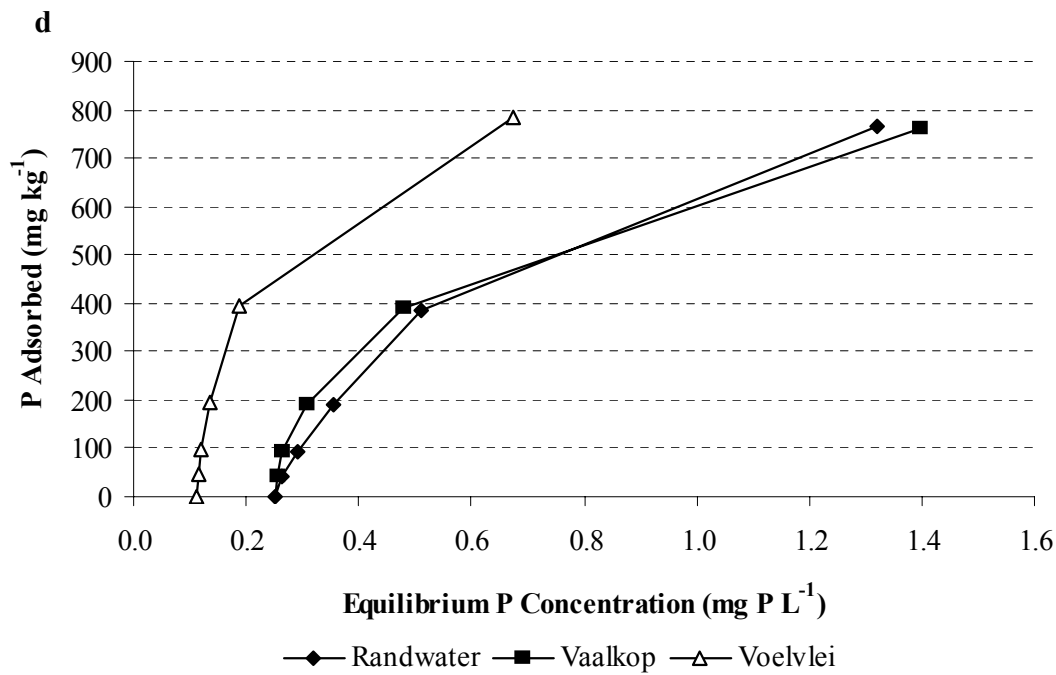
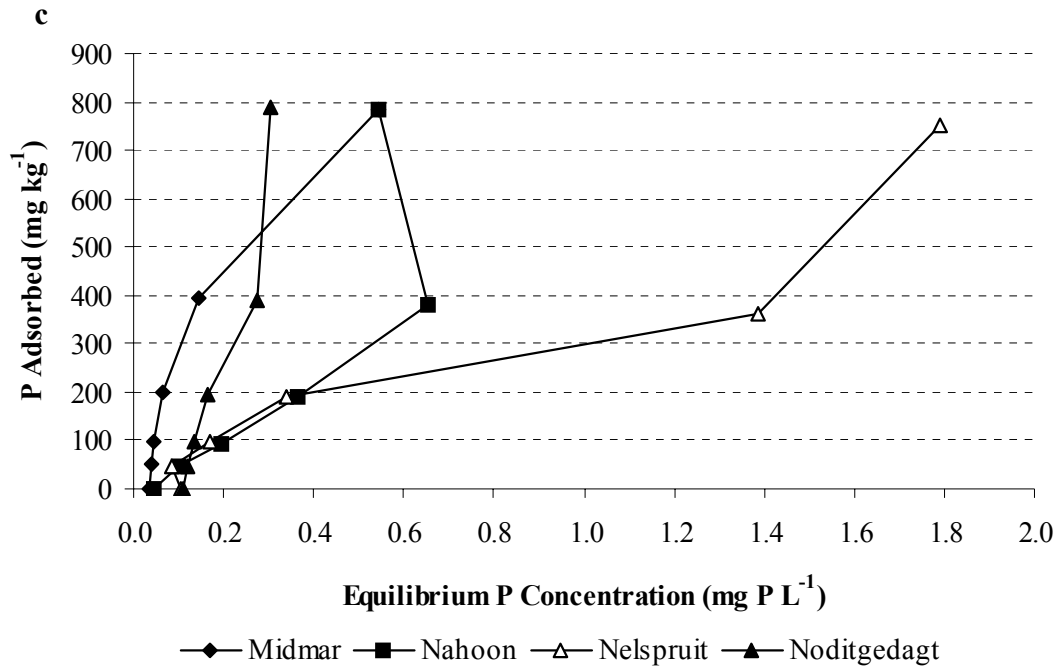
^a Dithionate extractable. ^b Oxalate extractable. ^c Pyrophosphate extractable. **OC** Organic Carbon.

^d Organic P is calculated as the sum of Bicarbonate P_o and NaOH P_o fractions.

Appendix 3.1 Phosphorus adsorption isotherms for (a) Blackheath, Bloemfontein, Bronkhorstspuit and Churchill and (b) Droogdam, Elandsjagt, Faure and Loerie WTRs at P applications of between 0 and 32 mg P L⁻¹



Appendix 3.1 continued Phosphorus adsorption isotherms for (c) Midmar, Nahoon, Nelspruit and Noditgedagt and (d) Randwater, Vaalkop and Voelvlei WTRs at P applications of between 0 and 32 mg P L⁻¹



Appendix 3.2 Amount (%) of P adsorbed at P applications of between 2 and 128 mg L⁻¹ for 15 South African WTRs

P App. Rate (mg L ⁻¹)	P Adsorbed (%)														
	Blackheath	Bloemfontein	Bronkhorstspuit	Churchill	Droogdam	Elandsjagt	Faure	Loerie	Midmar	Nahoon	Nelspruit	Noditgedagt	Randwater	Vaalkop	Voelvlei
2	94	97	88	95	87	94	94	95	98	95	96	94	87	87	94
4	97	98	94	97	93	97	97	98	99	95	96	97	93	93	97
8	98	98	97	96	96	98	98	99	99	95	96	98	96	96	98
16	99	98	98	96	98	99	99	99	99	96	91	98	97	97	99
32	100	99	99	98	99	98	99	99	98	98	94	99	96	96	98
64	98	95	98	94	98	96	98	99	97	94	94	96	97	96	97
128	97	95	99	94	97	95	97	98	96	94	93	95	96	96	95

Appendix 3.3 Correlation coefficients of four linear transformed empirical adsorption equations (Langmuir, Freundlich, Temkin and Linear) fitted to the phosphorus sorption data of 15 South African water treatment residues. Values in bold indicate models with the highest correlation coefficients that were selected to describe the sorption data

WTR	Langmuir		Freundlich		Temkin		Linear	
	P Resid. (mg L ⁻¹)	R ²	P Resid. (mg L ⁻¹)	R ²	P Resid. (mg L ⁻¹)	R ²	P Resid. (mg L ⁻¹)	R ²
Blackheath	0.118-0.161	0.723	0.118-0.161	0.948	0.112-0.161	0.996	0.112-0.161	1.000
Bloemfontein	0.059-0.340	0.271	0.059-0.340	0.941	0.046-0.340	0.998	0.046-0.340	0.957
Bronkhorstspuit	0.249-0.252	0.606	0.249-0.252	0.995	0.248-0.252	0.880	0.248-0.258	0.963
Churchill	0.103-0.615	0.129	0.103-0.615	0.968	0.096-0.615	0.973	0.096-0.615	0.970
Droogdam	0.266-0.321	0.585	0.266-0.321	0.848	0.264-0.455	0.975	0.264-0.455	0.955
Elandsjagt	0.114-0.214	0.425	0.114-0.214	0.962	0.112-2.508	0.964	0.112-0.214	0.914
Faure	0.123-0.167	0.705	0.123-0.167	0.939	0.115-0.167	0.998	0.115-0.167	0.999
Loerie	0.097-0.098	-	0.097-0.098	-	0.097-0.098	-	0.097-0.098	-
Midmar	0.04-0.147	0.075	0.04-0.147	0.872	0.037-0.544	0.996	0.037-0.147	0.930
Nahoon	0.102-0.654	0.988	0.102-0.654	0.999	0.043-0.654	0.862	0.043-0.654	0.998
Nelspruit	0.082-1.389	0.843	0.082-1.389	0.962	0.103-1.389	0.963	0.103-1.389	0.843
Noditgedagt	0.118-0.272	0.516	0.118-0.272	0.96	0.110-0.272	0.993	0.110-0.272	0.964
Randwater	0.265-0.509	0.869	0.265-1.320	0.822	0.253-1.320	0.993	0.265-0.509	0.984
Vaalkop	0.257-0.479	0.436	0.257-0.479	0.811	0.253-0.479	0.952	0.253-0.479	0.926
Voelvlei	0.115-0.187	0.535	0.115-0.187	0.986	0.112-0.675	0.950	0.112-0.187	0.956

Appendix 3.4 Correlation matrix showing the relationships between model parameters for those residues described by the Temkin equation and WTR chemical properties

	Ca	OC ^a	Ox ^b Al	Ox Fe	Dith ^c Al	Dith Fe	Pyr ^d Al	Pyr Fe	K ₁
K₁	0.83	-0.07	-0.22	0.90	-0.24	0.45	-0.27	0.53	
K₂	-0.09	0.14	0.01	-0.21	-0.04	-0.18	-0.02	-0.51	-0.48

^a Organic Carbon. ^b Oxalate extractable. ^c Dithionate extractable. ^d Pyrophosphate extractable.

Appendix 3.5 Correlation matrix showing the relationships between model parameters for those residues described by the Temkin equation and inherent P fractions

	Bicarb Pi	NaOH Pi	Po ^a	HCl Pi	P Resid.	P Ox	K ₁
K₁	0.79	0.96	-0.85	0.92	0.15	-0.17	
K₂	-0.17	-0.34	0.49	-0.31	-0.33	0.43	-0.48

^a Organic P is calculated as the sum of Bicarbonate P_o and NaOH P_o fractions.

Appendix 3.6 Water treatment residues chosen for further study in conjunction with the empirical isotherm equations used to predict the concentration of P required to give a desired residual P value. Extrapolation off the Loerie adsorption isotherm (Appendix 3.1 b) was used to estimate the required solution P concentration for this WTR

WTR	Best Fit Model	Equation	Parameters		Adsorption ^a		Desorption ^b		Sol. P Conc. ^c
			Slope (Affinity Parameter)	Intercept/constant	Predicted Conc.	P sorbed	Predicted Conc.	P sorbed	
					mg L ⁻¹	mg kg ⁻¹	mg L ⁻¹	mg kg ⁻¹	
Blackheath	Linear	$S = K_d \cdot c + a$	$K_d = 8072$	$a = -908$	0.150	298	0.131	149	6.2
Faure	Linear	$S = K_d \cdot c + a$	$K_d = 7726$	$a = -897$	0.150	262	0.133	131	5.4
Bloemfontein	Temkin	$S = K_I \cdot \log(K_2 \cdot c)$	$K_I = 444$	$K_2 = 21.5$	0.100	148	0.068	74.0	3.1
					0.200	281	0.096	141	5.8
					0.300	359	0.118	180	7.5
Midmar	Temkin	$S = K_I \cdot \log(K_2 \cdot c)$	$K_I = 651$	$K_2 = 29.2$	0.100	303	0.058	152	6.2
					0.200	499	0.083	250	10.2
					0.500	758	0.131	379	15.7
Randwater	Temkin	$S = K_I \cdot \log(K_2 \cdot c)$	$K_I = 1058$	$K_2 = 4.17$	0.300	103	0.268	51.5	2.4
					0.400	235	0.310	118	5.1
					0.500	338	0.346	169	7.3
					1.000	656	0.490	328	14.1
Nahoon	Freundlich	$S = K \cdot c^a$	$K = 599$	$a = 1.12$	0.100	45.4	0.054	22.7	1.0
					0.200	98.8	0.108	49.4	2.2
					0.500	276	0.269	138	6.0
Loerie	None	-	-	-	0.098	400	0.097	200	4.1

^a Values used in the P adsorption experiment. ^b Values used in P desorption experiment.

^c This value is based on the use of 0.5 g and 1.0 g residue for adsorption and desorption experiments respectively.

Appendix 3.7 Fractionation of P within 7 South African water treatment residues after the addition of sufficient P to give residual concentrations within the ranges predicted by three empirical adsorption isotherm equations (Appendix 3.6)

WTR	P Added mg kg ⁻¹	Percentage of Total P Fractionated							
		mg kg ⁻¹							
		Bicarbonate		NaOH		HCl	Residual P	P _{ox} ^b	P _{Tot} ^c
		P _i ^a	P _o ^a	P _i	P _o	P _i	P _i + P _o	P _i + P _o	mg kg ⁻¹
Blackheath ^L	0	0.34	22.3	0.41	24.2	1.13	51.6	73.7	1329
	303	0.67	15.3	2.08	14.1	0.73	67.1	60.8	1681
Faure ^L	0	0.34	22.3	0.41	24.2	1.13	51.6	57.2	1329
	262	0.43	13.0	1.17	17.2	1.18	67.1	70.3	1616
Bloemfontein ^T	0	0.91	27.3	0.50	27.4	1.91	41.9	71.3	1149
	148	1.49	19.2	1.13	17.1	1.51	59.6	52.2	1281
	281	1.77	19.5	1.07	19.8	1.66	56.1	63.6	1301
	359	1.94	20.4	1.27	18.2	1.54	56.7	64.7	1283
Midmar ^T	0	0.42	18.1	0.43	22.9	1.13	57.1	55.9	1416
	303	0.93	14.6	1.06	14.7	0.88	67.9	48.2	1744
	499	1.16	11.8	1.13	12.7	0.90	72.3	63.4	1774
	758	1.29	16.3	1.07	18.7	0.79	61.8	45.7	2119
Randwater ^T	0	0.34	20.5	0.30	21.1	1.31	56.4	31.8	1466
	103	0.66	14.7	0.69	16.5	1.07	66.4	22.0	1550
	235	0.84	12.9	0.69	13.8	1.08	70.7	33.0	1624
	338	0.96	13.5	0.74	20.5	1.11	63.2	33.1	1596
	656	1.18	22.5	0.71	19.6	1.00	55.0	28.4	1843
Nahoon ^F	0	0.47	26.6	0.46	26.5	1.03	44.9	42.8	1123
	45.4	0.63	21.8	0.96	20.6	0.79	55.2	15.9	1182
	98.8	0.67	20.2	0.92	15.5	0.74	61.9	28.2	1263
	276	0.79	25.9	0.84	15.6	0.65	56.1	33.9	1438
Loerie ^N	0	0.38	25.1	0.46	25.2	0.84	48.0	25.0	1280
	400	0.79	12.9	1.47	29.9	0.46	54.5	43.8	1722

^a P_i and P_o refer to the respective inorganic and organic components. ^b Oxalate extractable P.

^c Total P values were obtained from the sum of the of bicarbonate, NaOH, HCL and residual P fractions.

Sorption data described by ^L linear model, ^T Temkin model, ^F Freundlich model and ^N No model.

Appendix 3.8 The change (as %) in the distribution of P within 7 South African water treatment residues after the addition of P in accordance with 3 empirical isotherm equations (Appendix 3.6)

WTR	P Adsorbed	Bicarbonate		NaOH		HCl	Residual P	P _{ox} ^b	% P Unaccounted For ^c
		Pi ^a	Po ^a	Pi	Po	Pi	Pi + Po	Pi + Po	
	mg kg ⁻¹	Percentage Change in P as a Fraction of P Sorbed ^d							
Blackheath ^L	303	2.23	-12.9	9.64	-27.76	-0.87	144.51	13.50	-14.8
Faure ^L	262	0.93	-32.8	5.07	-16.63	1.56	149.42	140.78	-7.5
Bloemfontein ^T	148	5.93	-47.1	5.97	-65.82	-1.78	193.06	-103.32	9.8
	281	4.48	-21.5	2.92	-20.15	-0.16	88.72	2.93	45.7
	359	4.00	-14.6	2.89	-22.62	-0.62	68.03	3.09	62.9
Midmar ^T	303	3.41	-0.5	4.04	-22.25	-0.24	123.25	16.07	-7.7
	499	2.97	-9.3	2.81	-19.70	-0.01	95.54	67.07	27.7
	758	2.83	11.8	2.18	9.66	0.11	65.91	23.31	7.5
Randwater ^T	103	4.48	-62.2	5.31	-46.49	-2.19	173.04	-107.67	28.1
	235	3.48	-36.7	2.76	-34.85	-0.63	130.40	28.44	35.6
	338	2.94	-23.9	2.12	4.75	-0.40	51.67	17.42	62.9
	656	2.47	17.0	1.27	7.59	-0.10	27.60	8.29	44.2
Nahoon ^F	45.4	4.61	-87.6	13.10	-113.64	-4.76	314.16	-619.71	-25.8
	98.8	2.97	-43.4	6.13	-99.19	-2.20	262.79	-122.45	-27.1
	276	2.15	26.3	2.41	-25.62	-0.79	106.82	2.78	-11.2
Loerie ^N	400	2.27	-24.5	4.85	47.62	-0.71	80.49	108.09	-9.9

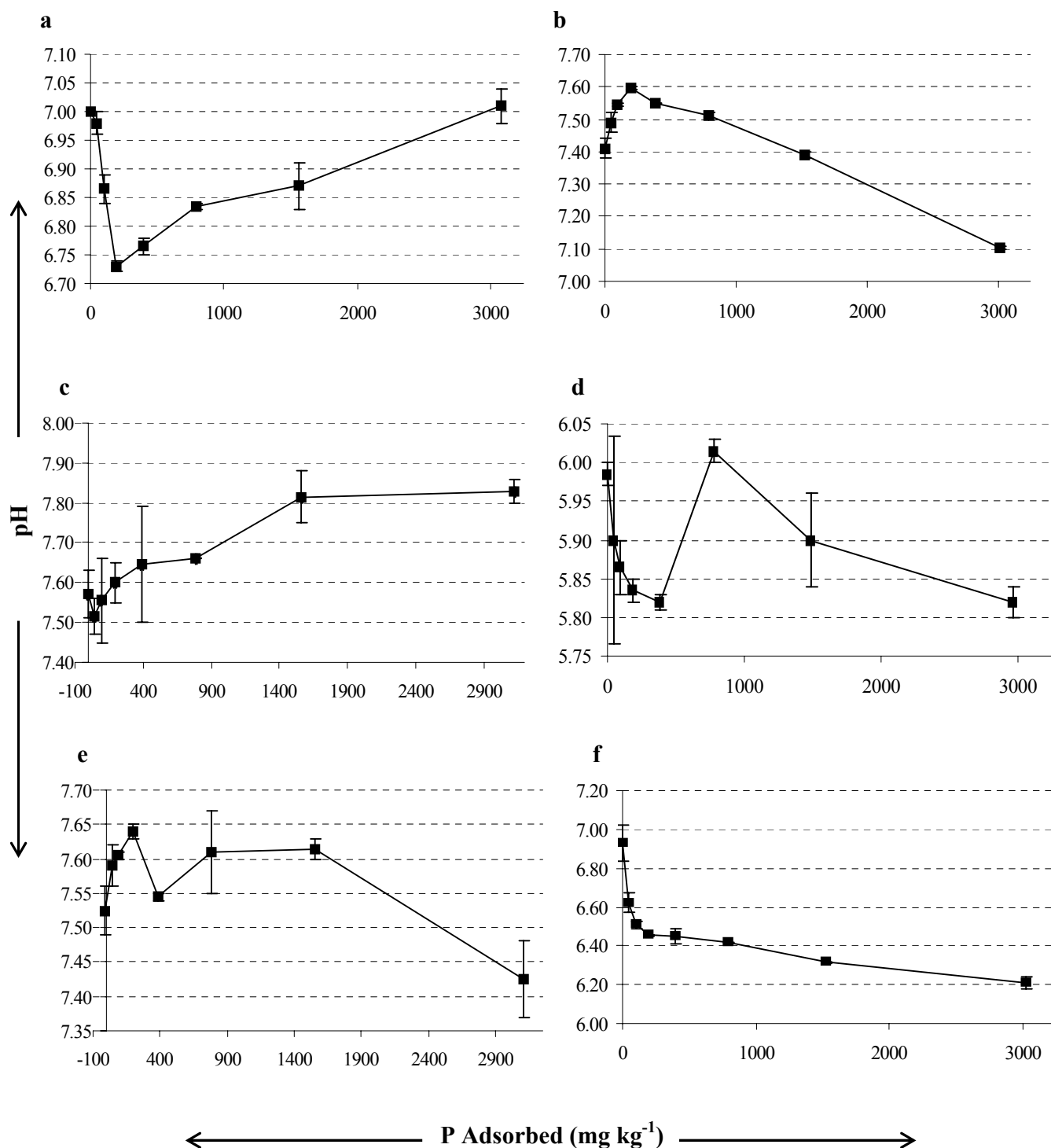
^a P_i and P_o refer to the respective inorganic and organic components. ^b Oxalate extractable P.

^c Percent recovery was calculated as the sum of the of bicarbonate, NaOH, HCL and residual P fractions.

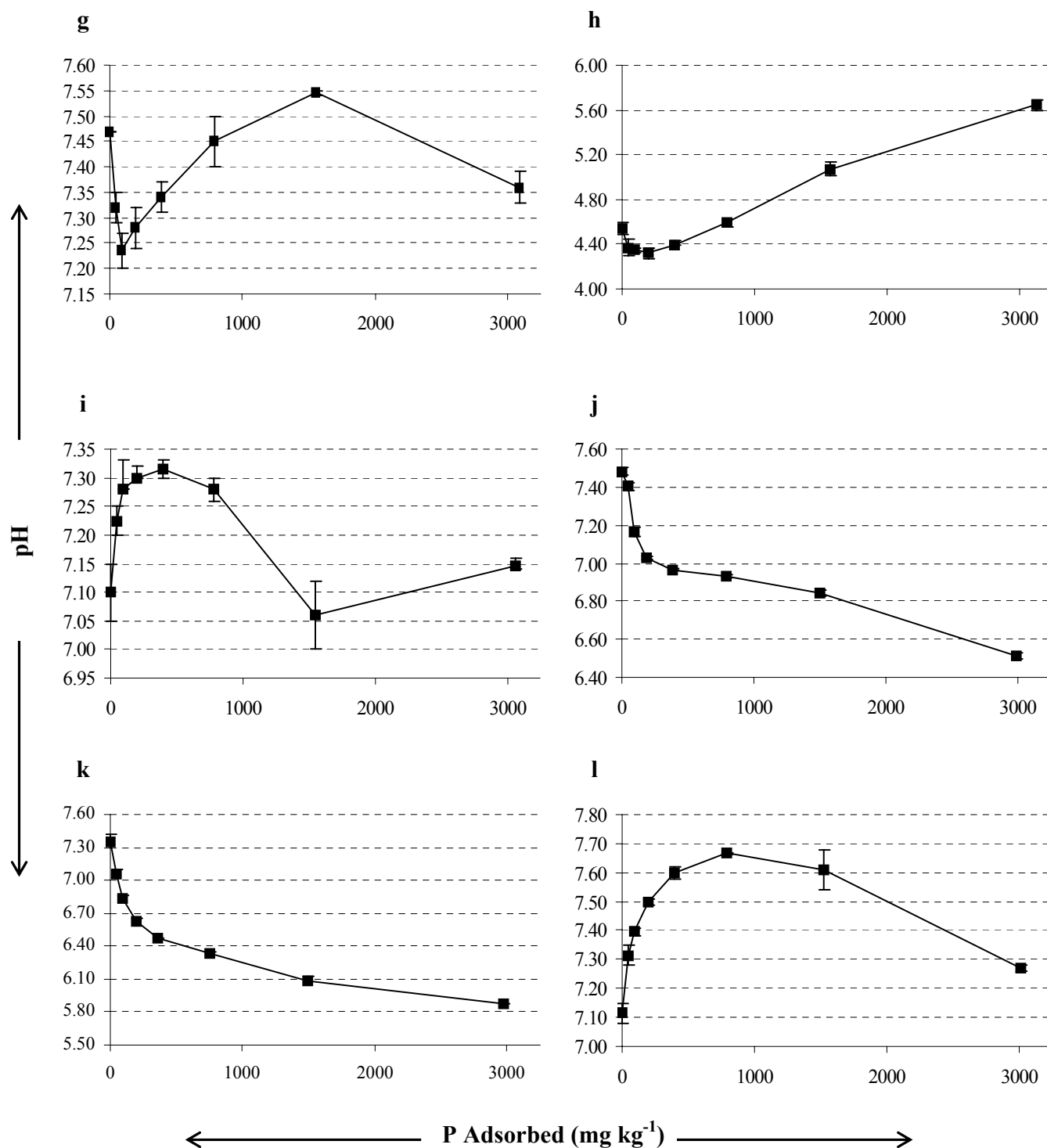
^d Percentage change = (Change in the quantity of P sorbed to a component / Total P sorbed) × 100.

Sorption data described by ^L linear model, ^T Temkin model, ^F Freundlich model and ^N No model.

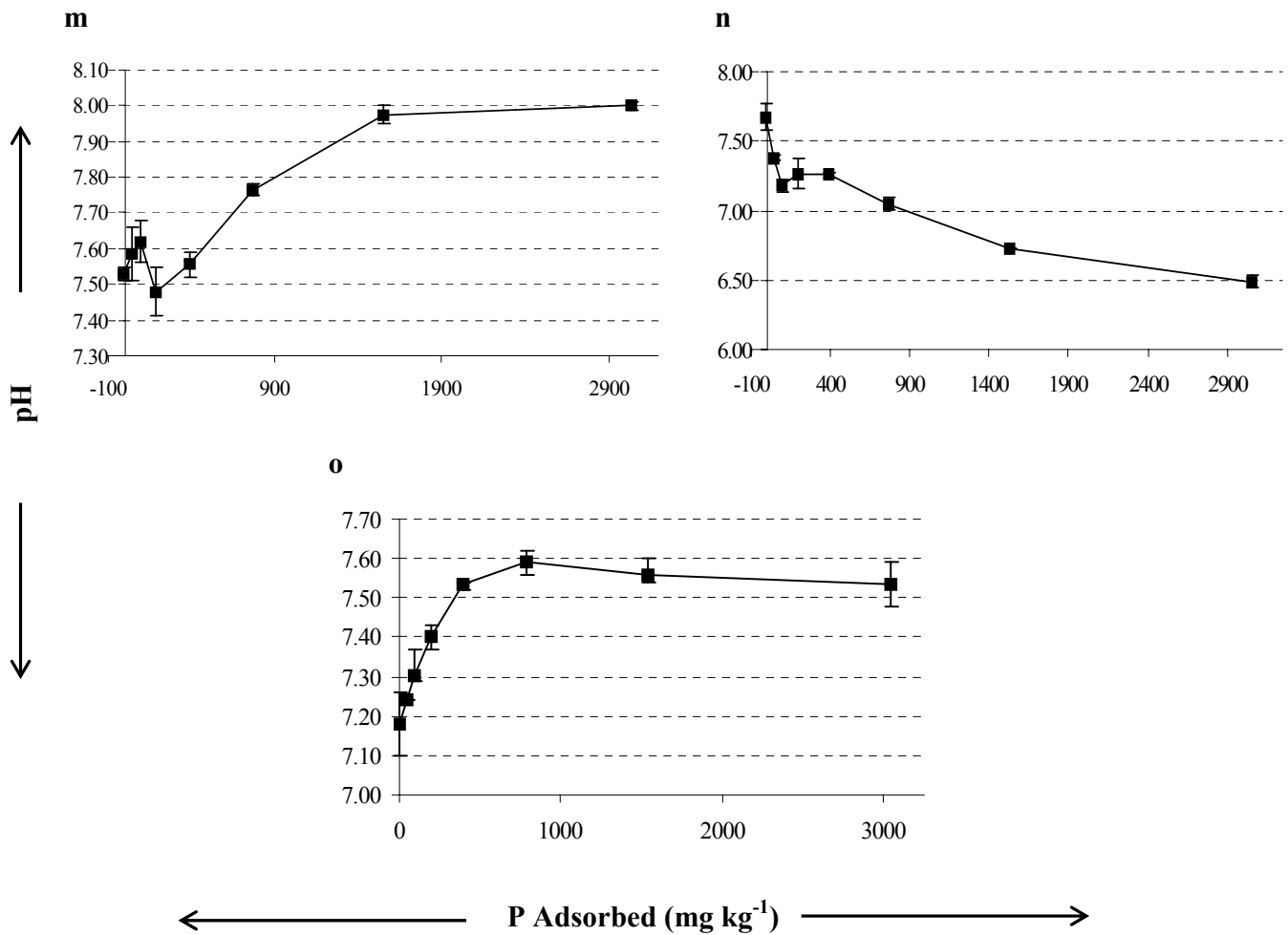
Appendix 3.9 Variation of supernatant solution pH with the quantity of P sorbed for (a) Blackheath, (b) Bloemfontein, (c) Bronkhorstspuit, (d) Churchill, (e) Droogdam and (f) Elandsjagt WTRs



Appendix 3.9 continued Variation of supernatant solution pH with the quantity of P sorbed for (g) Faure, (h) Loerie, (i) Midmar, (j) Nahoon, (k) Nelspruit and (l) Noditgedagt WTRs



Appendix 3.9 continued Variation of supernatant solution pH with the quantity of P sorbed for (m) Randwater, (n) Vaalkop and (o) Voelvloei water treatment residues



Appendix 3.10 Comparison of actual P sorbed to predicted sorbed quantities for 7 South African WTRs after the addition of P in accordance with three empirical isotherm equations

WTR	Experiment	Predicted		Actual P Sorbed		
		P Sorbed mg kg ⁻¹	Residual P mg L ⁻¹	Rep 1	Rep 2 mg kg ⁻¹	Av.
Blackheath ^L	Adsorption	303	0.150	304	300	302
	Desorption	149	0.131	152	151	152
Faure ^L	Adsorption	262	0.133	265	260	263
	Desorption	131	0.133	132	131	132
Bloemfontein ^T	Adsorption	148	0.100	145	138	142
		281	0.200	279	271	275
		359	0.300	357	360	358
	Desorption	74.0	0.068	72.2	71.1	71.6
		141	0.096	141	141	141
		180	0.118	183	182	183
Midmar ^T	Adsorption	303	0.100	303	296	300
		499	0.200	491	490	491
		758	0.500	757	754	755
	Desorption	152	0.058	152	151	151
		250	0.083	251	250	251
		379	0.131	385	387	386
Randwater ^T	Adsorption	103	0.300	116	111	114
		235	0.400	243	241	242
		338	0.500	348	347	347
		656	1.00	668	656	662
	Desorption	51.5	0.268	57.5	56.8	57.2
		118	0.310	123	123	123
		169	0.346	177	176	177
		328	0.490	340	342	341
Nahoon ^F	Adsorption	45.4	0.100	46.0	41.2	43.6
		98.8	0.200	102	98.0	100
		276	0.500	279	278	279
	Desorption	22.7	0.054	22.1	21.6	21.9
		49.4	0.108	51.1	50.4	50.7
		138	0.269	142	142	142
Loerie ^N	Adsorption	400	0.098	397	396	397
	Desorption	200	0.097	201	200	200

Sorption data described by ^L linear model, ^T Temkin model, ^F Freundlich model and ^N No model.

Appendix 4.1 Residual solution pH values for and the quantities of Al, Fe, Ca and P released from 15 South African WTRs after extraction with water, 20 mM bicarbonate, oxalate or citrate

WTR	Water					20 mM Bicarbonate					20 mM Oxalate					20 mM Citrate				
	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH
	 mg kg ⁻¹					 mg kg ⁻¹					 mg kg ⁻¹					 mg kg ⁻¹				
Blackheath	299	134	216	4.05	7.30	159	80.3	138	5.06	8.82	6325	120	529	12.0	4.40	10225	1126	1455	66.7	3.08
Bloemfontein	0	0	1368	7.29	7.40	0	0	983	18.3	8.58	0	2.22	905	102	3.39	409	1364	14405	195	4.71
Bronkhorstspuit	0	0	365	2.67	7.40	0	0	136	6.15	8.82	4211	45.8	692	12.0	4.90	307	335	1889	15.6	3.41
Churchill	0	0.0	1.45	1.61	6.42	18.9	7.14	16.7	3.06	8.88	5788	1703	72.0	9.67	2.76	623	184	120	5.14	2.66
Droogdam	0	0	975	6.74	7.31	0	0	1339	19.4	8.46	12.3	4.65	633	116	6.76	119	2318	10797	366	6.11
Elandsjagt	234	112	83.7	2.39	7.17	21.5	12.4	65.4	3.30	8.84	5106	313	369	5.83	3.74	2575	514	846	9.20	2.89
Faure	229	1744	356	8.93	7.47	102	1071	440	10.1	8.38	254	3300	349	4.41	5.01	581	19811	4419	13.7	4.20
Loerie	0	0	456	1.69	5.95	2341	675	64.8	14.4	8.69	7021	834	121	12.6	3.52	5244	1381	522	78.3	2.83
Midmar	0	0	941	4.19	7.31	0	0	592	7.94	8.65	672	753	408	18.6	5.89	1570	3392	3890	78.6	3.77
Nahoon	779	398	169	8.67	7.51	0	0	452	9.54	8.68	2291	4142	219	342	2.58	580	955	2052	51.5	3.07
Nelspruit	659	521	103	4.04	7.38	0	0	391	3.78	8.79	2004	2692	562	289	2.91	520	1169	1354	188	2.85
Noditgedagt	410	268	477	6.99	7.33	0	0	569	14.5	8.67	374	7014	812	39.1	4.28	540	10754	3368	666	3.04
Randwater	303	176	209	3.52	7.37	0	0	193	6.73	8.84	0	0	1066	3.38	8.31	261	729	19852	5.67	8.35
Vaalkop	0	0	853	1.66	7.39	0	0	695	3.25	8.38	1377	4210	369	28.8	2.30	374	1173	2087	13.9	2.89
Voelvlei	90.6	161	402	2.03	7.55	0	0	505	3.62	8.58	212	1957	378	3.25	5.26	330	5777	7231	5.48	3.91

Appendix 4.2 Correlation relationships between the changes in solution Al, Fe, Ca and P concentrations and solution pH (relative to a 1:25 water to WTR extraction) after extraction with 20 mM **(a)** bicarbonate, **(b)** oxalate and **(c)** citrate

a

	∂ Al	∂ Fe	∂ Ca	∂ P	∂ pH
∂ Fe	0.83				
∂ Ca	-0.58	-0.64			
∂ P	0.42	0.50	-0.11		
∂ pH	0.67	0.66	-0.33	0.11	
Ca ^a	-0.22	-0.28	0.37	0.51	-0.66
Ox Al ^b	0.07	0.23	-0.27	-0.19	0.31
Ox Fe ^c	-0.06	-0.43	0.35	0.09	-0.39

b

	∂ Al	∂ Fe	∂ Ca	∂ P	∂ pH
∂ Fe	-0.27				
∂ Ca	0.07	-0.01			
∂ P	-0.22	0.26	0.05		
∂ pH	-0.22	-0.49	0.23	-0.45	
Ca	-0.65	0.03	-0.40	0.12	0.24
Ox Al	0.66	-0.38	0.29	-0.31	-0.02
Ox Fe	-0.37	-0.05	-0.17	-0.21	0.28

c

	∂ Al	∂ Fe	∂ Ca	∂ P	∂ pH
∂ Fe	-0.18				
∂ Ca	-0.31	-0.01			
∂ P	-0.15	0.27	0.07		
∂ pH	-0.17	-0.05	0.88	-0.01	
Ca	-0.36	0.43	0.27	0.41	0.20
Ox Al	0.34	-0.31	-0.36	-0.30	-0.25
Ox Fe	-0.19	0.81	0.10	0.03	0.16

^a Exchangeable Ca.

^{b, c} Oxalate extractable Al and Fe respectively.

Appendix 4.3 Solution pHs for and the quantities of Al, Fe, Ca and P released from 7 WTRs pre-treated with P and extracted with water and 20 mM bicarbonate, oxalate and citrate

WTR	P Sorbed mg kg ⁻¹	Water					Bicarbonate					Oxalate					Citrate				
		Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH	Al	Fe	Ca	P	pH
		mg kg ⁻¹					mg kg ⁻¹					mg kg ⁻¹					mg kg ⁻¹				
Blackheath	0	299	134	216	4.05	7.30	159	80.3	138	5.06	8.82	6325	120	529	12.0	4.40	10225	1126	1455	66.7	3.08
	152	314	143	0	12.3	7.56	22.0	17.2	0	1.96	8.51	355	231	898	16.1	4.43	1311	120	1293	85.9	3.03
Faure	0	229	1744	356	8.93	7.47	102	1071	440	9.70	8.38	254	3300	349	4.41	5.01	581	19811	4419	13.7	4.20
	132	93.8	663	70.1	8.41	7.74	67.2	97.0	161	9.51	8.6	379	221	1416	3.14	4.73	252	7750	1116	10.2	4.03
Bloemfontein	0	0	0	1368	7.29	7.40	0	0	983	14.8	8.58	0	2.22	905	102	3.39	409	1364	14405	195	4.71
	72	476	316	291	17.9	7.73	3.45	2.64	566	22.1	8.63	0	0	876	5.87	6.63	344	1127	9865	168	4.56
	141	451	298	285	32.0	7.86	0	0	381	26.4	8.63	0	0	807	7.79	6.69	399	1231	11981	205	4.58
	183	398	259	283	37.7	7.89	0	0	303	26.8	8.66	0	0	910	9.43	6.73	372	1223	11065	219	4.57
Midmar	0	0	0	941	4.19	7.31	0	0	592	7.94	8.65	672	753	408	18.6	5.89	1570	3392	3890	78.6	3.77
	151	36.2	35.4	93.3	9.92	7.29	7.95	0	210	12.9	8.58	104	101	644	14.6	4.58	1417	3007	1601	48.3	3.65
	251	43.5	43.7	90.1	18.6	7.44	0	0	230	19.6	8.61	87.3	88.8	642	18.6	4.64	1540	3491	945	56.9	3.65
	386	85.1	74.4	77.2	28.6	7.47	0	0	173	25.9	8.59	89.7	92.3	661	29.0	4.60	1464	3311	1947	104	3.65
Randwater	0	303	176	209	3.52	7.37	0	0	193	6.73	8.84	0	0	1066	3.38	8.31	261	729	19852	5.67	8.35
	57	1116	923	110	20.2	8.31	14.9	13.4	36.7	6.79	8.63	0	0	2940	0.93	7.70	402	610	15384	11.0	7.53
	123	1003	638	69.0	17.1	8.56	10.0	6.27	184	20.2	8.74	0	0	2984	1.17	7.78	289	472	10338	14.7	7.65
	177	982	622	70.4	26.3	8.64	5.97	3.67	60.2	18.5	8.77	0	0	2965	2.74	7.80	386	281	7334	24.6	7.55
	341	1191	932	110	65.0	8.53	3.86	0	83.2	34.7	8.75	0	0	2959	17.6	7.81	288	668	17431	34.4	7.50
Nahoon	0	779	398	169	8.67	7.51	0	0	452	9.54	8.68	2291	4142	219	342	2.58	580	955	2052	51.5	3.07
	22	583	319	0	9.80	7.87	0	0	185	4.87	8.63	102	178	432	104	2.54	584	879	1209	25.1	3.01
	51	635	348	0	14.2	7.65	0	0	288	9.70	8.63	116	227	457	116	2.54	421	638	1124	30.5	3.00
	142	867	464	0	27.6	7.49	0	0	182	14.4	8.62	102	185	417	139	2.53	416	667	1375	51.6	3.03
Loerie	0	0	0	456	1.69	5.95	2341	675	64.8	9.74	8.69	7021	834	121	12.6	3.52	5244	1381	522	78.3	2.83
	200	4.06	0	0	0.93	6.51	0	467	21.2	12.2	8.23	374	818	160	25.4	3.51	5848	1475	111	76.3	2.81

Appendix 4.4 Amount (%) of P desorbed from 7 WTRs pre-treated with P and extracted with water (1:25 WTR:water ratio) and 20 mM bicarbonate, oxalate and citrate

WTR	P Sorbed mg kg ⁻¹	% Desorbed ^a			
		Water	Bicarb.	Oxalate	Citrate
Blackheath	152	7.93	1.25	9.83	39.4
Faure	132	5.98	6.71	2.30	7.04
Bloemfontein	71.6	22.7	24.6	3.39	63.1
	141	21.5	16.6	3.21	60.9
	183	19.9	13.4	3.32	57.9
Midmar	151	6.37	8.10	8.61	21.0
	251	7.30	7.59	6.89	17.3
	386	7.34	6.56	7.15	22.5
Randwater	57.2	33.3	10.6	1.54	17.5
	123	13.5	15.5	0.93	11.4
	177	14.6	10.1	1.52	13.5
	341	18.9	9.98	5.11	9.91
Nahoon	21.9	32.1	15.5	28.6	34.2
	50.7	24.0	16.1	29.5	29.8
	142	18.3	9.53	28.8	26.7
Loerie	200	0.46	5.68	11.9	27.4

^a % Desorbed = P desorbed / (P sorbed + P desorbed from untreated residue) × 100

Appendix 4.5 Changes in solution pH and the quantities of Al + Fe, Ca and P (mg kg⁻¹) released into solution for 7 WTRs extracted with bicarbonate, oxalate and citrate

WTR	P Sorbed mg kg ⁻¹	Bicarbonate				Oxalate				Citrate			
		Al + Fe	Ca	P	pH	Al + Fe	Ca	P	pH	Al + Fe	Ca	P	pH
		Change ^a				Change				Change			
Blackheath	0	-194	-77.5	1.01	1.52	6012	313	7.99	-2.90	10918	1239	62.7	-4.22
	152	-418	0	-10.4	0.95	129	898	3.74	-3.13	974	1293	73.6	-4.53
Faure	0	-801	84.3	1.40	0.91	1580	-6.22	-4.53	-2.46	18419	4064	4.78	-3.27
	132	283	90.9	1.10	0.86	-157	1346	-5.28	-3.01	7245	1046	1.83	-3.71
Bloemfontein	0	0	-385	7.51	1.18	2.22	-463	94.4	-4.01	1772	13037	188	-2.69
	72	-786	275	4.20	0.90	-792	585	-12.0	-1.10	679	9574	150	-3.17
	142	-749	96.9	-5.6	0.77	-749	522	-24.2	-1.17	880	11697	173	-3.28
	183	-658	20.5	-10.9	0.77	-658	627	-28.3	-1.16	937	10782	181	-3.32
Midmar	0	0	-349	3.74	1.34	1424	-533	14.4	-1.42	4962	2949	74.4	-3.54
	152	-63.7	117	3.00	1.29	133	550	4.72	-2.71	4353	1507	38.4	-3.64
	251	-87.2	140	1.01	1.17	88.8	552	-0.05	-2.80	4943	855	38.3	-3.79
	386	-159	95.5	-2.79	1.12	22.6	584	0.30	-2.87	4616	1870	75.7	-3.82
Randwater	0	-478	-16.1	3.20	1.47	-478	857	-0.14	0.94	512	19644	2.14	0.98
	57	-2011	-73.1	-13.4	0.32	-2040	2830	-19.3	-0.61	-1028	15274	-9.20	-0.78
	123	-1625	115	3.10	0.18	-1641	2915	-15.9	-0.78	-880	10269	-2.43	-0.91
	177	-1594	-10.2	-7.77	0.13	-1603	2895	-23.5	-0.84	-937	7264	-1.67	-1.09
	338	-2120	-26.8	-30.3	0.22	-2123	2849	-47.4	-0.72	-1167	17321	-30.6	-1.03
Nahoon	0	-1177	284	0.87	1.17	5255	50.2	333	-4.93	357	1883	42.8	-4.44
	22	-902	185	-4.92	0.76	-622	432	94.4	-5.33	561	1209	15.3	-4.86
	51	-983	288	-4.53	0.98	-640	457	102	-5.11	76.8	1124	16.2	-4.65
	143	-1332	182	-13.2	1.13	-1044	417	112	-4.96	-248	1375	24.0	-4.46
Loerie	0	3016	-392	8.05	2.74	7855	-335	10.9	-2.43	6625	65.7	76.6	-3.12
	201	463	21.2	11.3	1.72	1188	160	24.5	-3.00	7319	111	75.4	-3.70

^a This represents the difference in pH and elemental concentrations between the anion (oxalate, citrate and bicarbonate) and water extract.

Appendix 4.6 Correlation coefficients between the distribution coefficient (K_d) and solution pH for 15 South African WTRs

WTR	Best Fit Model	R² ^a
Blackheath	Linear	0.24
Bloemfontein	Temkin	0.96
Bronkhorstspuit	Freundlich	0.23
Churchill	Temkin	0.00
Droogdam	Temkin	0.88
Elandsjagt	Temkin	-0.76
Faure	Linear	0.00
Loerie	None	0.20
Midmar	Temkin	0.94
Nahoon	Freundlich	-0.56
Nelspruit	Temkin	-0.66
Noditgedagt	Temkin	0.87
Randwater	Temkin	0.00
Vaalkop	Temkin	-0.55
Voelvrei	Temkin	0.99

^a Correlation coefficients were determined up to the highest value of K_d which represents the points of inflection on the respective Scatchard plots (3.2.2).