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The effect of previous phosphorus additions to soils on phosphorus sorption and related parameters

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THE EFFECT OF PREVIOUS PHOSPHORUS ADDITIONS TO SOILS ON

PHOSPHORUS SORPTION AND RELATED PARAMETERS

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CERTIFICATION

I, Natasha L. Carlson-Perret, declare that this thesis, submitted in partial fulfillment of the requirements for the award of Masters of Environmental Science (research), in the School of Earth and Environmental Sciences, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Detrimental environmental effects resulting from the overuse of phosphorus (P) fertilisers in agriculture is a global issue which can cause the eutrophication of water systems. Phosphorus fertilisers are commonly used in Australia (and worldwide) and there remains no single simple model available which takes into account the many factors which affect P sorption and solubility; thus the potential for adverse environmental effects resulting from inefficient and excessive use is substantial.

In this study six Australian soils were analysed in order to ascertain the effect previous P fertiliser additions have on the behaviour of subsequent additions of P. In addition other physical and chemical factors affecting P sorption in soils were investigated in order to achieve a more 'complete' view of sorption across a range of soil types and under varying   conditions. Each of the six soils studied had five different rates of fertiliser (as triple superphosphate) applied two years prior to the commencement of this study. Phosphorus sorption experiments were conducted on the soils and the subsequent sorption data obtained was fitted to two commonly used sorption models, the Langmuir and Freundlich. Additional tests including pH, organic carbon content, mineralogy as well as other commonly used P extraction procedures were carried out.

All soils displayed effects on sorption of the new P additions as a results of the previous fertiliser treatments which had caused a residual 'pool' of P to remain in the soils, thus the higher the previous P additions, the less new P can be sorbed. The Langmuir model fit the data best, although acceptable R^2 values were also observed in the Freundlich curves. Chemical parameters also affected by the previous P additions were Colwell P, labile P and oxalate extractable P. Further research is still required in this field in order for a model which accurately describes P sorption in soils to be created.

ACKNOWLEDGEMENTS

CHAPTER 1 Introduction

Phosphorus (P) is a fundamentally important element in nature. It is required for many biological and chemical reactions and is an essential nutrient for biological organisms performing a vital role in the structure of RNA and DNA as well as cellular metabolism (Gilbert, 2009). Phosphorus also has significant industrial uses (for example, in detergents) and is extremely important in crop optimisation in agriculture where application to soil can lead to greater fiscal benefits for farmers (Tan, 2000; Gilbert, 2009; Bondre, 2011).

Phosphorus is a non-renewable resource found naturally at high concentrations in some minerals as well as in manures, the latter being the most economically exploitable sources of P (Bondre, 2011; Filippelli, 2011). The amount of available and economically viable P (in an engineering sense) is a much contested issue, what is agreed upon, however, is that reserves are limited (Gilbert, 2009; Bondre, 2011; Filippelli, 2011). Due to its many uses, P is in high demand globally and the fact that the many functions which it performs cannot be substituted by any other element; makes its purported declining availability so serious (Bondre, 2011). As a result, there is substantial global interest in minimising P losses from land application and the overuse of P fertilisers (that is, applications in excess of crop requirements) which result in no increase in crop productivity.

Human actions involving P, including the mining of P, and transport in fertilisers, animal feeds, crops and other products alter the global P cycle causing an accumulation of P in the soil (Figure 1-1) (Bennett *et al.*, 2001). The majority of

mined P-rich rock is turned into P fertilisers which have been in common use worldwide for many decades (Gilbert, 2009; Filippelli, 2011).

Slow inorganic   Rapid cycling organic and inorganic   Slow organic

Fertilizer   Plants   Animal waste

Primary P
minerals

Secondary P
minerals   Solution P   Microbial P   Chemically
and physically
protected
organic P

Occluded P   Labile and   Labile and
moderately labile   moderately labile
inorganic P   organic P

Figure 1-1: The phosphorus cycle; illustrating the relationship between phosphorus sources and the form it takes once in the soil (figure from Lewis and McGechan, 2002).

Australian soils are generally thought of as being P-poor as they are predominantly old having formed largely during the Tertiary period (Blair, 1983). Soil age combined with, but not limited to, parent material and leaching, are the principal elements contributing to the generally low fertility status of Australian soils (Blair, 1983). Consequently, farming practices in Australia rely on the use of P fertilisers to promote crop growth and high yields; P fertilisers can also have a detrimental environmental effect causing eutrophication of waterways, especially in close proximity to farms (Carpenter *et al.*, 1998; Sims and Pierzynski, 2005).

Due to the dramatic and ongoing demand for P, being able to ascertain how close a soil is to its optimal P loading is important, not only to prevent loss to waterways, but also for farmers for whom it has financial implications (Bondre, 2011; Filippelli, 2011). Consequently, any research which can help mitigate P losses from agricultural sources has a threefold effect:

•mitigating the incidence of eutrophication;

•reducing P wastage; and,

•providing potential economic incentives for the farming community to use less P.

Therefore, formulating a way to define and measure the optimal P concentration of a particular soil (and can consequently be applied to soils in general) which adheres to all of these factors is an incredibly important area of research. It has the potential to provide data to assist in the development of more proficient management plans for the mitigation of eutrophication worldwide. In order to achieve this however, we must better understand the complex chemical, physical and biological factors which impact on the sorption properties of P in soils.

1.1 Phosphorus - Soil Interactions

This section presents an overview of on the behaviour of P in soils. More in depth discussion on particular aspects relevant to this study is presented in the literature review (Chapter 2).

The binding of P to soil particles is a complex phenomenon and is commonly referred to as sorption, which is the term used when the exact mechanism for

the retention of a sorbate is unknown (Sims and Pierzynski, 2005). Sorption of P may include bonding to the external surface of a particle as well as inclusion within the particle and can be caused by both physical or chemical processes (Sims and Pierzynski, 2005).

Phosphorus is found in soils in a variety of different forms, for example, as inorganic and organic complexes (as discrete 'particles' or bound to other species) present in the soil solution, sorbed to the solid fraction and bound 'within' the solid phase (Correll, 1998; Sims and Pierzynski, 2005). Sorption of P to soil particles occurs via a biphasic mechanism (Barrow, 1978; Correll, 1998; Sims and Pierzynski, 2005). The initial stage is very rapid, characterised by nonspecific adsorption and ligand exchange with mineral edges and the short range order crystalline states of iron (Fe) and aluminium (Al) oxyhydroxides and calcium carbonates (depending on soil type and chemical factors) (Barrow, 1978; Sims and Pierzynski, 2005; Rayment and Lyons, 2011). Three types of ligation can occur; monodentate, bidentate and binuclear, with monodentate forms being appreciably more reversible than the other forms (Sims and Pierzynski, 2005). The subsequent reaction occurs at a much slower rate and consists of the movement of P via diffusion into the internal regions of the particles as well as surface precipitation and polymerisation of P on to mineral surfaces (Barrow, 1978; Correll, 1998; Sims and Pierzynski, 2005).

The dominant forms of P in a soil are dependent on many variables including, soil type (parent material, mineralogy), age, the biological component of the soil and numerous chemical parameters such as pH, organic matter content, redox potential and the abundance/availability of metal complexes (especially Fe and

Al) as well as any ions which compete for P binding sites (Sims and Pierzynski, 2005; Janardhanan and Daroub, 2010; Zou *et al.,* 2011). The age of a soil can impact considerably upon sorption affecting factors like pH, the concentration of calcium (Ca) and organic carbon and increasing the bonding between P and Fe and Al species (Sims and Pierzynski, 2005; Zou *et al.,* 2011). Sorption is generally high in soils rich in clay and reactive oxyhydroxides and is influenced by the chemical and physical properties of these, for example, their mineralogy and crystallinity (Beckwith, 1965; Bolland *et al.* 1996; Sims and Pierzynski, 2005; Agudelo *et al.,* 2011; Janardhanan and Daroub, 2010; Kerr *et al.* 2011; Rayment and Lyons, 2011).

Due to the complex nature of the soil matrix and the wide variety of soil types globally, as well as localised differences within a soil subgroup, developing a single chemical test to determine the P concentration which will satisfy the chemical/biological requirements of a soil means it is not straight forward. This and historical reasons explain why there are a range of soil P tests (including Labile P and Olsen P) and others which have a specific geographical context (such as Colwell P in use in Australia and Bray P in parts of the US).

1.2 Environmental Impacts of Phosphorus Use

A surfeit of P in water systems can lead to eutrophication which impacts on all areas of life within and dependent on that water body, as well as the catchment system as a whole. Eutrophication causes an expansion of biological activity which can deplete available oxygen until the water system becomes anoxic (Carpenter *et al.,* 1998).

It has been known for some time that P can be lost from soils by leaching and surface runoff (Hart *et al.*, 2004). Phosphorus can be considered to enter the environment via two types of runoff - avoidable and unavoidable (Hart *et al.,* 2004; Dougherty *et al.,* 2011a). Avoidable runoff occurs when soils are so saturated with P from either the use of fertilisers and the specific and/or intentional application of manures and is followed shortly by a period of precipitation, subsurface leaching and/or surface runoff (Dougherty *et al.,* 2011a). Alternatively unavoidable runoff occurs when soil P is near optimal concentration and runoff follows within days of unintentional manure or fertiliser deposition via grazing and livestock activity (Dougherty *et al.*, 2011a).

Agriculture and its associated practices are widely accepted as one of the largest non-point sources of P leading to eutrophication worldwide. Agriculture is usually described as a non-point source of P contamination (Carpenter *et al.*, 1998; Bennett *et al.*, 2001). Transport of P from agricultural sources is typically intermittent and linked to factors such as seasonal variability and soil characteristics. These factors render non-point sources more difficult to control than point sources (such as waste treatment plants) which tend to give relatively stable and continual P outputs (Carpenter *et al.*, 1998; Bennett *et al.*, 2001).

It has long been known that agricultural processes and fertilising cause P issues in local aquatic environments (Agudelo *et al.,* 2011). Synthetic fertilisers provide an 'available' source of inorganic P which is easily taken up by flora; available P sources are either 'loosely' bound to the soil particle (for example, labile P) or dissolved in the soil water which makes them vulnerable to being transported into aquatic systems (Rayment and Lyons, 2011). Concentrations of P in soil

solution can vary dramatically from less than 0.01 mg P/L (characteristic of infertile soils) to as much as 1 mg P/L and can even reach as much as 7-8 mg P/L in highly fertilised soils (Tan, 2000; Sims and Pierzynski, 2005). However, relatively low levels of P (such as 0.01 – 0.03 mg dissolved P/L and 0.035-0.10 mg total P/L) in the same range as those necessary for terrestrial plant growth can have a negative effect on water systems (Correll, 1998).

The fact that eutrophication is globally widespread and such a damaging issue for water systems means that any inroads which can be made to reduce the most prolific sources of aquatic P are important. Eutrophication is a significant global environmental problem and remediation is a time demanding and expensive process (Sims and Pierzynski, 2005).

1.3 Significance of This Research

Much previous research has been undertaken in Australia on the effects of successive P applications to soil (for example, Barrow and Campbell, 1972; Fisher and Campbell, 1972; Probert, 1985; Bolland *et al.,* 1996). However, such research has predominantly concentrated on the bioavailable forms of P affecting crop yields. A gap in the research exists in that much less work has been carried out on the relationship(s) between previously sorbed P, its effect on the sorption of subsequent applications of P and what this means in terms of the fertilisation necessary to supply plant requirements. Most researchers agree that it is important to take a strategic and multi-faceted approach to agricultural P management that incorporates the determination of sorption capacity, the agricultural requirement of the soil (for example, is the land used for crop or livestock production as well as environmental and climate considerations

(Carpenter *et al.,* 1998; Blake *et al.,* 2000; Borda *et al.*, 2011). This is too great a task to be undertaken in this project, thus this research attempts to address the knowledge gap identified above; to clarify the effect of previous P application on the sorption of subsequent P additions and how that relates to important chemical and physical soil parameters. The results will be displayed in an easily accessible format for potential incorporation into future applications in the mitigation of eutrophication as well as more efficient and economical uses of P.

1.4 Aims

There are four aims of this research;

• Determine the effect of previous P fertiliser treatment on the sorption behaviour of subsequent P additions.

• Investigate the effect of previous P fertilisation on soil characteristics (pH, organic carbon content, available forms of P and on of oxalate extractable Fe, Al and P).

• Examine the impacts that chemical variables have on the P sorption capacity of the soil (pH, organic matter and Fe and Al oxyhydroxide concentration).

• Ascertain whether the main factors controlling P adsorption can be modeled by a simple mathematical model.

CHAPTER 2 Literature Review

Chapter 2 presents an overview of previous research that has been undertaken in this field with consideration of the importance of P in agriculture, P behaviour in soils and P sorption models.

2.1 Phosphorous in Agriculture and its Impacts

Across differing soil types there are varying degrees of P sorption capacity. Consequently, different types of soils will need to be treated in different ways in regard to the amounts of fertilisers or manures required for optimal plant and animal production (Rayment and Lyons, 2011). The P status of a soil is of the utmost agricultural importance, as too little P may reduce crop yields and therefore livestock production below economically viable levels. Conversely, saturation of the soil by P may result in excessive leakage of P into waterways where it can contribute to eutrophication.

Worldwide, P fertilisers are commonly used in farming. Phosphorus is often the limiting nutrient in a system and farming practices, by their very nature, remove P from the soil. As a result, P needs to be restored to maintain productivity. A surplus of P in agricultural soils can occur if more nutrients are added to soils than are removed in crop or livestock production (Figure 2-1) (Carpenter *et al.*, 1998). Much work has been carried out on P and its sorption properties in soils (Svensson and Söderlund, 1976; Tiessen,1995); nonetheless, a widely applicable model which accurately predicts the P requirements of soils in all their complexity is yet to be developed. Consequently, the potential for sub- or

supra-optimal soil P concentrations and their associated problems is substantial.

Figure 2-1: Depiction of common phosphorus inputs and outputs in a variety of agricultural practices (figure from Carpenter *et al.,* 1998).

Agricultural practices cause P to be lost from the soil via an array of pathways including run off, erosion and 'export' in cropping and livestock production (Figure 2-1). Bennett *et al.* (2001) estimates that the net global P storage in terrestrial and freshwater ecosystems has increased by at least 75% since the industrial revolution, with the majority coming from agriculture. The use of P fertilisers is especially prolific in Australia due to the low P status of the majority of soils (Figure 2-2) (Blair, 1983). In many places liming of agricultural soils is very common. The practice of introducing liming agents to acid soils serves to make P held in the solid phase become more available for the following reasons: the binding sites for the orthophosphate ion become more negatively charged, ions that bind strongly with P are precipitated (such as Fe and Al) and the surface charge of Fe and Al oxyhydroxides become increasingly negative (McBride, 1994; Sims and Pierzynski, 2005). In soils with a high Ca

concentration, P availability can actually decrease as Ca species are precipitated as Ca-P compounds (McBride, 1994; Sims and Pierzynski, 2005).

Figure 2-2: Phosphorus fertiliser amendment rates for Australia between 1992-1996 (data and figure from National Land and Water Audit, 2001, (www.anra.gov.au)). Where markers indicate where soils used in this study originated. The orange marker indicates the Flaxley soil, collected in South Australia and the green marker indicates the general area where all other soils were collected in NSW (Glenmore, Richmond, Robertson, Bowral and Camden).

A major cause of P loss from soils (both particulate and dissolved) is from large overland flow events often catalysed by storms (Carpenter *et al.*,1998; Correll, 1998; Blake *et al.,* 2000; Hart *et al.,* 2004; Trangsubkul *et al.,* 2005; Sims and Pierzynski, 2005; Owens and Shipitalo, 2006; Agudelo *et al.*, 2011; Borda, *et al.,* 2011). In highly fertilised pastures P is largely lost in solution via overland or subsurface flows rather than as a constituent of particulate matter from erosion

(Carpenter *et al.*,1998; Correll, 1998; Blake *et al.,* 2000; Hart *et al.,* 2004; Trangsubkul *et al.,* 2005; Owens and Shipitalo, 2006; Borda, *et al.,* 2011). Surface runoff is the more detrimental form of mobilised P to waterways as it can contain higher concentrations of P than subsurface flow (Loganathan and Hedley, 1997; Owens and Shipitalo, 2006). Overland flow may not exclusively caused by rain events; 'flooding' style irrigation techniques can cause loss by both overland flow and percolation to groundwaters (Tilman *et al.,* 2002; Toor *et al.,* 2004). These large scale irrigation practices commonly employed in crop farming (for example rice) can carry pesticides, nutrients and salts and potentially deposit them into water systems via seepage into ground water or direct flow into waterways (Tilman *et al.,* 2002). For this reason, researchers have suggested the use of drip or pivot irrigation systems which not only decrease the potential for P loss from the soil but also decrease salinization; unfortunately, these methods are not yet economically viable for large scale food crops (Tilman *et al.,* 2002). The amount of P calculated as lost from surface runoff and subsurface flow may not be enough to cause economic concern to farmers (with typical losses of less than or equal to 0.15 kg and up to 2.0 kg of dissolved reactive P per hectare) but these small amounts may be sufficient to cause eutrophication (Sims and Pierzynski, 2005; Tilman *et al.,* 2002; Owens and Shipitalo, 2006). Consequently, without strong recommendations from environmental regulators there is little incentive to adopt improved practices.

It can be difficult, in many cases, to determine the exact cause of P accession into waterways at a specific location as there are many factors which can contribute to the increase of P during storm flow events, such as, direct losses

from fertiliser soon after application (Agudelo *et al.*, 2011). As well as increasing the potential for particulate P loss via erosion, the removal of crops also interrupts the P cycle via the removal of a P sink and as plants are removed there is less of a physical barrier to limit the movement of overland flow (Carpenter *et al.,* 1998; Lewis and McGechan 2002; Tilman *et al.,* 2002; Owens and Shipitalo, 2006). This presents a strong case for the protection of riparian vegetation as both a sink and a physical barrier to mitigate P loss to waterways (Carpenter *et al.*, 1998; Bennett *et al.*, 2001; Lewis and McGechan, 2002; Tilman *et al.,* 2002; Owens and Shipitalo, 2006). Thus, long-term field studies are invaluable for illustrating the potential P loss for a particular soil and region, and incorporate 'real life' variables, such as, abnormal weather events, seasonal changes and the long term effects of agricultural practices (Blake *et al.,* 2000; Owens and Shipitalo, 2006).

The sediments of a water body can, and do, contribute P to the water system as well as binding some P (depending on the composition of the sediment). Agudelo *et al.,* (2011) found that the values of dissolved reactive P in stream water during storm flow were comparable with the equilibrium phosphorus concentration (EPC_0) of field sediments, indicating that overland flow of water had occurred and impacted the stream P concentration. The EPC_0 value is the solution concentration where neither net sorption nor desorption occur (Vaananen *et al.*, 2008). Soils and sediments with a higher EPC_0 have an increased potential to release P (Vaananen *et al.*, 2008). The sediments of water bodies usually have lower labile P values compared with those of the field soils surrounding them (Agudelo *et al.*, 2011). This indicates that an equal

amount of field soil would contribute more P to the water system than the same amount of resuspended river/stream sediments (Agudelo *et al.*, 2011).

The use of land is an important factor in the potential for P transmission to waterways; for example, wool and meat production in Australia is predominantly carried out on unfertilised land with the only real impact from these low productivity activities being a build up of P at watering loci stock camps and feed lots; predominantly from animal faeces (Blair, 1983; Soinne *et al.*, 2008). It was thought that farms used principally for livestock production were perhaps less likely to cause damage to the environment via P initiated eutrophication as less fertilisation is required for grazing livestock than for cropping (Owens and Shipitalo, 2006). However, P saturation is often found where livestock production occurs, not just due to manure deposition, as areas with higher animal grazing may aid surface runoff of P as grazing animals deplete vegetation (Owens and Shipitalo, 2006). If manures are not removed, this can cause significant amounts of P being moved into the soil solution in these localised areas (Carpenter *et al.*, 1998; Borda, *et al.*, 2011). Consequently, It is important when testing for P in soils that the organic/plant available P is not ignored, especially on low P soils where the only sources may be from crop residues or manures (Sims and Pierzynski, 2005).

Whilst the proportion of available P may be greater in soils fortified with animal manures than in their inorganic fertilised counterparts, the latter remain a significant P source due to their sheer size and usage (Sims and Pierzynski, 2005; Agudelo *et al.*, 2011). That is, environmental risk is a function of both intensity and area, huge areas used for cropping which often have P fertiliser

applied in, at times, copious amounts representing a far greater potential environmental threat than localised manure deposition. The continual application of both synthetic fertilisers and manures can cause an accumulation of P in soils in a variety of inorganic and organic forms (McDowell and Condron, 2000). By the time water resources are noticeably impaired, P accretion in terrestrial soils and upstream sediments may already be P-rich enough to maintain high loading to lowland aquatic systems for some time (Bennett *et al.*, 2001).

2.2 Phosphorus Behaviour in Soils

Interactions of P in both natural and managed soil ecosystems are largely dependent on the form in which P is present whether they be organic, inorganic, microbial, bound to other species or as free anions, and the complex interactions between them (Condron and Newman, 2011). Other anions can compete with P for sorption sites on soil particles causing more P to remain in the soil solution where it is bioavailable, and as such has a greater potential to be transported into water systems (Lewis and McGechan, 2002; Sims and Pierzynski, 2005). The most common anions which compete with P for sorption sites are sulfate, hydroxide, silicate, molybdate and organic species, including carboxylate ions, such as, oxalate; the degradation products of crop residues and manures may also bind to these sorption sites (Sims and Pierzynski, 2005). The orthophosphate ion is usually quite tightly bound to the soil mineral binding sites, and any competition is only really an issue if the concentration of these competing anions in the soil solution is high relative to orthophosphate (Sims

and Pierzynski, 2005). Nonetheless, anion competition may contribute to seasonal variation in the concentration of P in surface runoff.

The environment in which the soil is located impacts on how P is mobilised and transported. For example, runoff from grasslands or forested areas contains less sediment than runoff from 'bare' soils due to the physical barrier of the plants, consequently less erosion occurs, therefore the predominant loss is via dissolved P (Carpenter *et al.,* 1998; Lewis and McGechan, 2002; Tilman *et al.,* 2002; Owens and Shipitalo, 2006). Leaching of dissolved P into groundwater occurs via much more complex pathways than that of surface runoff; such as, transmission via soil micropores, percolation and fracture flow. Thus, land used for cropping (which uses more P fertiliser) is a complex P source from which P loss can be much harder to control (Lewis and McGechan, 2002). The relative proportion of soil P in inorganic and organic forms can vary greatly and mobility depends on the interaction between the properties, nature of the flow and soil chemical conditions (McDowell and Sharpley, 2001).

2.2.1 Phosphorus and pH

The pH of both the solid and liquid matrices of the soil can impact the sorption of P by affecting the protonation and deprotonation of functional groups and surface binding sites (Sims and Pierzynski, 2005). These effects alter the electronegativity of the surfaces of soil particles; a relationship commonly referred to as the adsorption envelope (Sims and Pierzynski, 2005).

Due to their age, most Australian soils are usually P limited and are often highly weathered and acidic (Blair, 1983). An acidic soil environment causes the 'fixing' of P within the solid phase of the soil as phosphate solubility is predicted to decline as pH decreases (McBride, 1994; Tan, 2000). The P present in acidic soils is largely comprised of the inorganic phosphate ions; $H_2PO_4^-$ and HPO_4^{2-} much of which is complexed with other species on the surface of the soil particles via ion exchange, for example, the binding of P to Fe and Al oxyhydroxides (McBride, 1994; Tan, 2000). The binding of P to calcium carbonate species occurs more in alkaline soil environments not as common in Australia (McBride, 1994; Tan, 2000). This research will focus on the interactions of acidic soils as all soils tested had pH values <5.6.

The pH of the soil directly affects the charge of the orthophosphate species in solution and consequently P sorption; with the majority of P in soils having surfaces which are negatively charged. In acid soils, $H_2PO_4^-$ is the dominant ion while at a more neutral pH of 6-7 both $H_2PO_4^-$ and HPO_4^{2-} are present in comparable concentrations; above pH 7, HPO_4^{2-} is the predominant species (PO_4^{3-} is also present in small quantities) as illustrated below (Tan, 2000).

•$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ $pK_a1 = 2.17$

•$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$ $pK_a2 = 7.31$

•$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$ $pK_a3 = 12.36$

The pH of soil, soil solution and aquatic systems is usually between 2.17 and 12.36 (pK_a1 and pK_a3), and does not usually reach either extreme (Tan, 2000). This is why the most common phosphate ions present in these environments

are $H_2PO_4^-$ and HPO_4^{2-} (Tan, 2000). In most soils, the concentrations of these ions are generally low and are commonly in the region of 1 mg/L or less (Tan, 2000).

2.2.2 Phosphorus - Iron and Aluminium Oxyhydroxide Interactions

Phosphorus reacts readily with metallic species and in highly weathered acidic soils, Fe and Al oxyhydroxides are the dominant species with which P interacts (Tan,2000; Sims and Pierzynski, 2005; Ahmed, *et al.,* 2008; Rayment and Lyons, 2011). Oxyhydroxides of Fe and Al may be present as discrete minerals, distinct surface layers on soil particles or in complexes with the organic fraction of the soil (Sims and Pierzynski, 2005). These short-range crystalline oxyhydroxides (sometimes referred to as amorphous) are well known to affect P sorption in soils (for example, see Bolland *et al.,* 1996; Ahmed *et al.,* 2008; Vaananen *et al.,* 2008; Janardhanan and Daroub, 2010). Iron and Al oxyhydroxides are good indicators for P sorption as they act as a sink for soluble phosphates. Iron enriched concretions are major sinks of P often controlling the dynamics of P in agricultural soils and maintaining a high sorption capacity (Hamon and McLaughlin, 2002; Gasparatos *et al.,* 2006, Vaananen *et al.*, 2008).

In acidic environments, typical of many Australian soils, adsorption of P occurs principally via the formation of an inner-sphere complex between orthophosphate anions, (such as $H_2PO_4^{2-}$), and a metal cation or metal oxyhydroxide, such as Fe or Al, subsequently causing P fixation (Tan, 2000; Sims and Pierzynski, 2005). In this process, the orthophosphate ion undergoes ion exchange with OH^- or H_2O groups on the soil particle surface with a

coordinate covalent bond forming between the P atom in the phosphate ion and the metal cation (Sims and Pierzynski, 2005). This, in turn, decreases the point of zero charge (PZC) (when there are no charged groups present on the particle and thus, it effectively has no charge) of the surface of the soil particle due to an increase in negative charge density (Sims and Pierzynski, 2005). As a soil becomes substantially more weathered, the oxyhydroxides of Fe and Al become more crystalline resulting in a decrease in P sorption capacity as it is the poorly crystalline forms which are involved in P sorption (Sims and Pierzynski, 2005). This process of Fe/Al - P fixation can also take place in alkaline soil environments but to a much lesser extent (Sims and Pierzynski, 2005).

The relationship between Fe and Al oxyhydroxides and P sorption is well known which is why the oxalate extractable Fe and Al tests are favoured by researchers as it extracts the poorly crystalline oxyhydroxides of Fe and Al and not the crystalline forms which are not associated with P sorption (Rayment and Lyons, 2011). Oxalate extractable Fe and Al was one of the parameters analysed in this study in order to characterise P sorption in the soils tested due to this well known relationship, as well as most of the natural P in the surface of Australian soils is presumed to be bound to Fe oxides because of the strong correlation between the P and Fe content (Norrish and Rosser, 1983).

2.2.3 Phosphorus and Organic Matter

The amount of organic P found in soils is ordinarily less than the inorganic P content but can range widely (between 13-90% of soil P) depending on the soil type (McDowell and Sharpley, 2001). The primary sources of organic P in soils are from the decomposition of organic detritus from biota and animal

excrement, which yields a host of compounds including phospholipids, nucleic acids, inositol phosphates and carboxylic acids as well as humus (Tan, 2000). The low P sorption capacity of organic dominated soils is due to the coating of aluminosilicate clay minerals and metal oxyhydroxide species by humic and fulvic molecules which reduce the availability of binding sites for phosphate ions. As a consequence, an increased proportion of P present in such soils is biologically available (Blake *et al.*, 2000; Sims and Pierzynski, 2005; Owens and Shipitalo, 2006; Borda *et al.,* 2011).

Due to high weathering rates and low rainfall, Australian soils usually do not have a high concentration of organic matter, although this may not be the case in the agricultural sector as manures are often either not removed from grazing pastures or may be placed on the land purposely. Decaying organic matter on the surface of a soil can provide a source of 'instantly labile' P, which is rapidly incorporated into the soil and soil solution and which can then be easily transported via leaching to lower horizons (Vaananen *et al.*, 2008).

Most studies agree that P rich fertilisers (such as superphosphate and NPK), work most efficiently in conjunction with manures rich in phosphates and organic matter (Blake *et al.,* 2000; Toor *et al.*, 2004; Borda *et al.,* 2011). The organic matter contained in the manure acts, as noted earlier, to compete with P for binding sites causing the P to remain in the soil solution for uptake by plants, whilst also making it more vulnerable to transportation into water systems (Toor *et al.,* 2004; Sims and Pierzynski, 2005).

Application of organic matter, whilst making P more available to crops and enhancing yields, has also been found to contribute to the risk of eutrophication

in surface waters due to the increased ability of P to be easily transported whilst it remains in the soil solution (Carpenter *et al.,* 1998; Borda, *et al.,* 2011). For this reason, high rainfall events have been found to be one of the greatest problems relating to P runoff and so it is recommended that fertilisers (either synthetic or organic), should not be applied when high rainfall is predicted to occur within the days following application (Carpenter *et al.,* 1998; Blake *et al.,* 2000; Owens and Shipitalo, 2006; Borda *et al.,* 2011). The effects of adding organic matter to soils (such as manures, crop remains and other biosolids), has been researched and contradictory results have emerged, depending on the kind of organic matter employed as well as the chemical and physical parameters of the soil to which it is applied (Sims and Pierzynski, 2005). McDowell and Sharpley (2001) found that more P was determined as desorbable P for soils amended with fertiliser compared with those treated with manure, this implies that the P derived from manures is less desorbable than that in fertilisers; this stands to reason as fertilisers are applied to soils to increase crop yields so the P needs to be in an 'available' form. Thus, as mentioned previously, the organic content of the soil should not be overlooked when determining P sorption (even if synthetic fertilisers are more commonly used), especially in low phosphate soils where the only sources of P may be from crop residues or manures (Sims and Pierzynski, 2005).

2.3 Sorption Isotherms

Sorption isotherms are mathematical representations of the relationship between the concentration of P which is sorbed by soil particles and the amount remaining in solution after a known amount of P has been added (Figure 2-3)

(Bache and Williams, 1971; Rayment and Lyons, 2011). Two models extensively used in P research are the Langmuir and Freundlich isotherms (Zou *et al.*, 2011).

Figure 2-3: A general P sorption curve with sorption (x) plotted against equilibrium phosphorus concentration (c), depicting the characteristic shape observed in P sorption experiments where the 'plateauing' of the curve indicating the soil is nearing its sorption maximum. (figure from Bache and Williams, 1971)

2.3.1 The Langmuir Model of Sorption

The Langmuir model was originally developed for gas adsorption and enables the calculation of a P sorption maximum or P_{max}, whereas the Freundlich assumes an infinite adsorption capacity (Gunary, 1970; Lewis and McGechan; 2002; Sims and Pierzynski, 2005; Zou *et al,.* 2011).

The Langmuir P_{max} corresponds to the state when all the sorption sites on a soil particle have been filled (Ahmed *et al.*, 2008). The Langmuir approach also incorporates a constant 'k' value which is related to the P bonding energy (Gunary, 1970; Lewis and McGechan; 2002; Sims and Pierzynski, 2005; Zou *et al.,* 2011). The Langmuir model is represented by the equation

$$c/x = c/x_m + 1/kx_m \qquad\qquad [1]$$

Where x_m represents the adsorption maximum (Bache and Williams, 1971). The Langmuir isotherm incorporates numerous assumptions many of which are implausible for soils as their individual characteristics are so complex and varied (Gunary, 1970; Sims and Pierzynski, 2005). For example;

- bonding energy is independent of the density with which P covers the surface and of the site of adsorption

- adsorption energy can differ from site to site,

- that multiple layer (not just monolayer) coverage of the surface may be possible and;

- the sorption equilibrium is not always easily reversible (Bache and Williams, 1971; Campbell and Davies, 1995; Sims and Pierzynski, 2005).

Theoretically, the graphing of c/x against c should yield a straight line (Bache and Williams, 1971). In practical experimentation, this plot usually yields a slight curve (Figure 2-4) which serves to illustrate that not all of the assumptions inherent in the Langmuir model are applicable to P sorption in soils; for instance the bonding energy is not constant, meaning there is no well defined maxima

(Bache and Williams, 1971; Campbell and Davies, 1995; Lewis and McGechan, 2002). Despite these failings, the Langmuir model is still widely used in soil research, (particularly P soil work) and is often useful in conjunction with other models, such as, the Freundlich.

Figure 2-4: The differences between; (**i**) the slightly curved line usually observed in experimental procedures from a plot of c/x against c (Langmuir sorption model) and (**ii**) what is expected (a straight line). (figure from Bache and Williams, 1971).

2.3.2 The Freundlich Model of Sorption

The Freundlich isotherm is a purely mathematical construct based on the theoretical idea that as the density of the sorbate increases the energy of adsorption decreases (Bache and Williams, 1971). This is the premise which makes it applicable to the binding of a charged species (such as P) to solids with charged surfaces; which is why it is so popular in this research field (Gunary, 1970; Bache and Williams, 1971). The Freundlich equation is

$$x = ac^{1/n} \qquad\qquad [2]$$

In this form, a and n are constants. The basic equation [2] can be modified as;

$$\log x = \log a + 1/n \log c \qquad\qquad [3]$$

The plotting of log x against log c should produce a straight line; however, most soil sorption experiments fitted to a Freundlich isotherm usually exhibit a slight curve (Bache and Williams, 1971; Campbell and Davies, 1995). As discussed in 2.3.1 (in relation to the Langmuir model) this curvature reflects the fact that the Freundlich may not accurately describe soil-P interactions. It has been documented that many researchers do not believe that either the Freundlich or the Langmuir give a precise characterisation of the P/soil quantity/intensity relationship (Bache and Williams, 1971; Fitter and Sutton, 1975).

Despite these failings, the Langmuir and Freundlich models are still widely used in soil P research. Fitting soil data to both models may aid in giving a more accurate picture of the soil P interactions in the soils tested.

This literature review has indicated that despite a very large body of research having been completed on P in the environment, we still do not possess a comprehensive understanding of all the processes and contributing factors involved. In particular the behaviour of sequential additions of P is less well understood and, while the factors influencing changes are well known, the details of interaction require more attention. This study is an attempt to add to our understanding of the issues.

CHAPTER 3 Materials and Methods

Chapter 3 outlines information on the materials and methods used in this study including soils, sample handling and processing, laboratory procedures and data processing.

3.1 Soil Samples and Sample Processing

Six soils were sampled for this analysis, Richmond (D), Camden (KA), Glenmore (MO), Bowral (MA) and Robertson (RO) from south eastern New South Wales, and Flaxley (FL) from the Fleurieu Peninsula, South Australia (Table 3-1). Soil classification and texture were described by Dougherty *et al.,* (2011b) and are represented in Table 3-1. Bulk samples of topsoil (0-10 cm) from each site were sampled in 2009 as described in Dougherty *et al.,* (2011b). These soils were used in previous studies by Dougherty *et al.* (2011b) and were treated as follows. The soils were cleaned of large organic matter, such as roots, and sieved (<6 mm) before varying amounts of triple superphosphate (TSP) were added to give P additions ranging from 0-2158 mg/kg (depending on soil type). The varying rates were designed to achieve 10 fold differences in soil P from optimal to excessive. The soils were used in pasture growth studies in which approximately 500 g of each soil were packed into small plots and sown with 25 kg/ha ryegrass (*Lolium perenne*). Trays were subjected to wetting and drying cycle studies via rainfall simulations at 45 mm/h until 30 minutes after leaching had commenced. When experimentation was concluded, samples were air-dried and stored indoors for a period of 2 years.

As much biological material as possible was removed from the soils in preparation of the subsequent procedures. For this study, five sub-samples

Table 3-1: Soil classification and texture (Dougherty *et al.*, 2011b).

Soil ID	Soil Type (Isbell, 1997)	Particle Size Analysis (%)		
		Silt	Clay	Sand
Camden (KA)	Brown Chromosol	17	31	53
Flaxley (FL)	Brown Chromosol	19	29	52
Glenmore (MO)	Red Chromosol	34	43	23
Bowral (MA)	Brown Kurosol	30	43	27
Richmond (D)	Red Kandosol	5	10	85
Robertson (RO)	Red Ferrosol	19	54	27

across the varying TSP additions of each soil type were taken from the surface 10 mm of the air dried plots in April 2011. Any remaining large plant or root matter was removed and samples ground to pass through a 1mm sieve. Further sub-samples were taken and soils were ground to pass a 250 μm sieve which were used for organic carbon and X-ray diffraction analysis.

3.2 Laboratory Methods

3.2.1 Mineralogy

Samples were analysed by X-ray diffraction in the School of Earth and Environmental Science at the University Of Wollongong. Samples were crushed to the appropriate size (4 μm) and analysed by a Phillips 1130/90 diffractometer with Spellman DF3 generator set to 1 kilowatt achieved by setting the diffractometer to 35 Kv and 28.8 Ma. The samples were analysed under the following parameters; range = 4° - 70° 2-θ at 2° per minute with a step size of 0.02. After analysis, traces were produced via a GBC 122 control system and analysed using the programs Traces, UPDSM and SIROQUANT (Mandile and Hutton, 1995).

3.2.2 pH Analysis

Post-equilibration with P and centrifugation of the soil suspensions, the pH of the clear supernatant was measured on a Thermo Orion 3 star pH meter (Ross electrode) at a soil:solution of 1:10 (0.01 M $CaCl_2$) slightly modified from the procedure described by Rayment and Lyons (2011) in which the soil:solution ratio is 1:5.

3.2.3 Organic Carbon Content

The organic carbon content of the soils was determined via the Walkley-Black procedure as per Nelson and Sommers (1996). 0.2 - 0.8 g of <250 μm soil samples were weighed and samples digested with 10 mL of potassium dichromate standard (0.1667 M) and 20 mL of concentrated sulphuric acid. The excess dichromate was then titrated against a standardised Fe(II) solution. An unreacted carbon correction factor of 1.3 was used to compensate for any undigested organic carbon.

3.2.4 Labile Phosphorus

Labile P was determined at the CSIRO Land and Water Division Laboratory, Waite Campus, University of Adelaide using their ^{32}P-PO$_4$ E value protocol. Briefly, soil samples (2 g) were weighed into 50 mL centrifuge tubes before 20 mL of deionised water and 1 drop of toluene were added. All samples were equilibrated for 24 hours on an end-over-end shaker. After the equilibration period, the pH was measured and the soil suspensions spiked with ^{32}P -PO$_4$ (0.5 kBq/mL). Suspensions were then equilibrated on the shaker for a further 24 hours and centrifuged at 3500 rpm for 20 minutes followed by filtration through a 0.2 μm filter. The filtrates were analysed using beta counting and colorimetric P tests. The analysis and calculation of the E-values were performed using the method of Bertrand *et al.,* (2003).

3.2.5 Oxalate Extractable Phosphorus, Iron and Aluminium

1.0 g soil samples (<0.5 mm) were placed in 250 mL containers and 100 mL of acid oxalate reagent added. Samples were shaken end-over-end for 4 hours in

the dark. Suspensions were then centrifuged, the supernatant diluted with CsCl solution and element concentrations read via ICP-MS (Rayment and Lyons, 2011). Analyses were carried out at the CSPB Laboratories, Western Australia.

3.2.6 Colwell Phosphorus

Colwell P results for these soils were provided by previous analysis as described in Dougherty *et al.*, (2011b) via the method of Rayment and Lyons, (2011). 100 mL of extracting solution ($NaHCO_3$ at pH 8.5) was added to 1.0 g of air dried soil (<2 mm); samples were equilibrated on an end-over-end shaker for 16 hours. Soil suspensions were centrifuged and filtered and aliquots of the supernatant taken. 2 mL of 1 M H_2SO_4 were added and mixed and a further 5 mL was added once effervescence ceased and the solution left to sit overnight. Aliquots of the solutions were taken and 8 mL of colour reagent added (Murphy and Riley, 1962). After 30 minutes the absorbance of the solutions were read via spectrophotometer at 882 nm.

3.2.7 Phosphorus Sorption Measurements

Sorption was determined as outlined in the procedure; '9J1 phosphate sorption curve - manual colour' as described by Rayment and Lyons, (2011). Soil samples were suspended in a 0.01 M $CaCl_2$ at a soil:solution ratio of 1:10 and suspensions shaken end-over-end for 17 hours with varying, known amounts of added P (0-5 mg) as K_2HPO_4 dissolved in 0.01 M $CaCl_2$. Post-equilibration samples were centrifuged at 300 N/minute (3000 rpm) for 3 minutes (Hettich Universal 30F rotor E1174). Samples were filtered through Whatman GF/C 1.2 μm filters and aliquots taken immediately for determination of molybdate reactive P left in solution using a modified version of the method of Murphy and

Riley (1962), which uses ascorbic acid as the reducing agent. Phosphorus remaining in solution was determined via absorbance reading at 882 nm (Shimadzu UV1700 - spectrophotometer) and calibration curve. The amount of P sorbed by each individual soil sample was calculated from the difference of the amount of P remaining in the soil solution and the known amount of P added as described below in Section 3.3.

3.3 Data Processing and Statistical Analysis

Using the program 'Numbers' (Apple for Macintosh) the data obtained from above (3.2.7) were used to produce the sorption curve for each soil according to the following calculations;

mg of P in 50mL solution = mg P remaining in solution x (50 mL ÷ aliquot volume mL) [4]

P adsorbed (by 5g sample) = initial P added - [4]   [5]

P adsorbed/kg = [5] x (1000 ÷ accurate weight of soil sample g)   [6]

Equilibrium Concentration mgP/L = [4] x (1000 mL ÷ 50 mL)   [7]

The values of equation [6] were plotted against [7] in order to generate sorption curves.

The EPC_0 of each soil was determined by solving the equation of the line of best fit applied to the sorption curves, for when y=0 (or the x intercept) (Appendix II).

A correlation matrix was synthesised involving all the variables measured (excluding mineralogy) and the P value for each correlation calculated (Table 4-3).

Sorption values were also fitted to the Langmuir and Freundlich sorption isotherms (equations [1] and [3]) which are used to compare different soils and estimate the P sorption maximum of each soil.

Lines of best fit were applied to the sorption curves as well as the Freundlich and Langmuir plots using the Apple program Numbers. The first point of each curve was excluded from both the Langmuir and Freundlich curves in order to ascertain the best fit straight line (as the first point in all cases represented desoprtion not allowed for in the Langmuir model; and not able to have a log applied in the case of the Freundlich).

CHAPTER 4 Results and Discussion

Chapter 4 presents the data obtained from the experimental procedures carried out over the term of this project. I intend to present the data in the following sequence, QA/QC followed by results of laboratory based methods with sorption data last in order to give an overall view of the results obtained and how they relate to P sorption.

4.1 QA/QC

Appropriate quality control measures were carried out in this project to ensure the accuracy of the results reported.

4.1.1 pH

The pH meter was calibrated each day before use according to the specifications as set out in the instrument manual. Two buffers bracketing the range of expected pH (pH 4 and pH 7 Orion- Thermo Scientific) were used to calibrate the meter with a slope value of >96 deemed as acceptable.

4.1.2 Organic Carbon

When undertaking the organic carbon procedure internal reference samples of known value were used. An internal reference soil sample of known concentration (EMAI - PIT) and at least one replicate of each sample type (6 in total) was carried out with each batch to verify accuracy of results. Agreement with reference values was acceptable at ± 10%.

4.1.3 Oxalate Extractable Phosphorus, Iron, Aluminium and Labile Phosphorus

When samples were sent for analysis at external laboratories, duplicate samples were included as well as samples of 'known' value, all replicates values returned good accuracy and precision (± 10%). In the case of the labile P analyses (carried out by the CSIRO), three water blanks and three water standards (to be spiked with known quantities of a standard) were prepared by the analyst.

4.1.4 Sorption Measurements

The spectrophotometer was calibrated using a full range of concentrations of a P standard made from the primary standard KH_2PO_4. Check standards at either end of calibration range were checked every day before use in order to determine if the calibration was drifting. At least two replicate samples were performed for each sample type, one at a low added P concentration and another at a high added P concentration. These were repeated if they did not agree within ±10% of the original sample.

4.2 Results

4.2.1 XRD Analysis

The SIROQUANT analysis results revealed that all of the soils were found to have a large portion of their composition as quartz, ranging from 81% in the D soils to 32% in the RO soils (Table 4-1).

The other major components of the analysis were the clays illite and kaolin as well as the minerals goethite (an Fe oxyhydroxide) and gibbsite (an Al hydroxide) (Table 4-1). As mentioned earlier in Section 2.2.1 and later in Section

Table 4-1: Mineralogical composition of studied soils (XRD). Where the soils are represented as KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; D - Richmond; RO - Robertson.

Soil	Quartz	Albite	Orthoclase	Kaolin	Chlorite	Muscovite	Illite	Mixed layer	Gibbsite	Goethite
					% Composition					
KA	78	3		8		2	3	3	1.5	1.5
FL	78	5	1.5	9			6	<1		
MO	58	1		20		7	6	7	1	1
MA	66	<1		15	2	3	6	5	1.5	1.5
D	81	1	11	3		1	2	<1		
RO	32	3	5	17		12	5	8	10	7

4.2.2, all studied soils are acidic (pH < 5.6) In highly weathered and acidic soils P sorption is controlled by 1:1 clay minerals, such as, kaolinite and halloysite, and oxyhydroxides of and Fe (goethite) and Al (gibbsite) (Sims and Pierzynski, 2005). Clays and minerals (such as kaolin and gibbsite) facilitate the binding of P within the soil (Beckwith, 1965; Bolland *et al.* 1996; Sims and Pierzynski, 2005; Agudelo *et al.*, 2011; Janardhanan and Daroub, 2010; Kerr *et al.* 2011; Rayment and Lyons, 2011) and indeed, there is a general relationship between Fe, Al and P in Australian surface soils (Norrish and Rosser, 1983).

The D soils were observed to have the highest percentage quartz (81%) as well as a large orthoclase fraction (11%), very little kaolin (3%) and no goethite (Table 4-1) and displayed a course sand-like texture. This is indicative of a low sorbing soil as there are not many surfaces appropriate for P binding. Sandy type soils have the lowest P sorption capacity due to the lower content of binding sites (Sims and Pierzynski, 2005) as further discussed in Section 4.2.6. The RO soils are perhaps the most diverse in their mineralogy and have the highest amount of reactive materials (that is; goethite - 7%, gibbsite - 10%, muscovite - 12% and kaolin - 17%) which indicate the high potential for P sorption as mentioned above (Table 4-1).

4.2.2 Soil pH Analysis

The pH of soils was found to vary between the different soil types, but all were acidic; they ranged from 4.25 (1:10 $CaCl_2$) for MA soils to 5.26 (1:10 $CaCl_2$) for FL (Table 4-2).

There was a general increase in pH observed over the range of increasing fertiliser additions but no larger than 0.34 (found in the D soils) (Table 4-2).

Table 4-2: Soil chemical parameters of six Australian soils. Where soils are D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson.

Soil	Tray No.	P added mg/kg	Colwell P mg/kg	Oxalate Fe mg/kg	Oxalate Al mg/kg	Oxalate P mg/kg	Labile P mg/kg	Organic C %	pH (CaCl2) 1:10
D	2	0	48	917	1767	135	9.79	1.24	4.96
D	4	1098	346	944	1924	665	74.63	1.17	5.30
D	6	81	66	805	1602	146	16.98	1.09	5.02
D	8	234	97	810	1646	275	31.68	1.13	5.28
D	11	610	256	792	1636	446	54.71	1.02	5.14
KA	1	0	41	3196	2244	227	22.30	2.98	5.13
KA	5	90	74	3111	2132	290	32.22	3.02	5.29
KA	8	260	144	3256	2210	394	47.50	2.95	5.29
KA	11	599	277	3673	2358	701	80.50	3.29	5.39
KA	15	1047	318	3814	2409	1052	106.80	2.74	5.48
FL	2	0	85	2999	3730	333	29.41	3.50	5.26
FL	4	96	99	3230	3805	369	35.36	3.42	5.40
FL	9	286	150	3248	3200	509	50.66	3.38	5.38
FL	12	658	237	3716	3757	777	88.70	3.87	5.51
FL	15	1150	290	2773	3559	1189	116.40	3.54	5.54
MO	2	0	75	5951	6086	477	36.87	3.42	4.83
MO	5	1248	391	6049	6179	1404	160.94	3.35	4.99
MO	6	71	112	5904	5711	539	46.98	3.39	4.87
MO	9	348	210	5832	5645	759	73.58	3.63	4.99
MO	11	602	206	5930	5579	882	90.04	3.43	4.99
MA	1	0	19	4293	7460	157	3.76	4.78	4.25
MA	3	55	29	4280	7779	197	8.33	4.71	4.43
MA	7	188	80	4546	7990	363	35.42	4.46	4.40
MA	11	604	198	4651	8110	941	103.88	4.60	4.54
MA	15	1322	503	4500	8223	1795	227.75	4.56	4.54
RO	1	0	34	10363	11940	614	5.11	6.11	4.33
RO	3	79	54	9824	12200	760	12.17	6.13	4.31
RO	6	306	105	10555	11710	1425	40.75	6.23	4.34
RO	10	1038	334	10704	12410	2030	178.75	6.48	4.43
RO	15	2158	896	11243	13840	2952	385.70	6.10	4.57

Previously added P did not have much of an effect on the pH of the new P

additions it just served to supply the soils with a slightly higher 'starting' pH

value (Table 4-2). This is further illustrated by there being no significant

correlation between pH and previously added P (> P 0.05) (Table 4-3).

The pH measured after equilibration of the soils with the new P additions

showed minor changes (of no larger than 1 pH value) over the range of

concentrations, soil pH usually increased after additions with new P (data not

presented here as too large). Complexion of P at mineral surfaces is expected

to increase pH as it displaces OH^- (as discussed in Section 2.2.1).The change

in pH is a function of the soil pH buffering capacity not measured here however,

previous research has found that pH effects on P sorption in acid soils (of

around 4.3) are very minor (Bache and Williams, 1971).

pH values were found to give very good correlations with oxalate extractable Fe

and Al (P <0.01) (Table 4-3). This may be due to Fe and Al oxyhydroxides being

some of the dominant P binding species in acidic soils (Tan,2000; Sims and

Pierzynski, 2005; Ahmed, *et al.,* 2008; Rayment and Lyons, 2011). Bolland *et*

al., (1996) found that oxalate extractable Al and pH were both reasonably well

related to the phosphorus buffering capacity (or PBC) and as such were

recommended as the procedures to best estimate P sorption in the S-W

Australian soils studied.

There was a good correlation observed between pH and organic carbon (P

<0.01) (Table 4-3). The amount and form in which organic content is present

within a soil can impact the pH as discussed in Sections 2.2.1 and 2.2.3.

Table 4-3: Correlation matrix depicting correlation coefficients for all parameters as well as the corresponding P value

Parameters	P added mg/kg	Colwell P mg/kg	Oxalate Fe mg/kg	Oxalate Al mg/kg	Oxalate P mg/kg	Labile P mg/kg	Organic C %	pH (CaCl$_2$ 1:10)	Pmax mg/kg	Slope of Freundlich plots	Intercept of Freundlich plots	EPC$_0$ mg/L
P added mg/kg	1.000	0.963 P = <0.001	0.240 P = 0.201	0.248 P = 0.186	0.864 P = <0.001	0.928 P = <0.001	0.161 P = 0.395	0.069 P = 0.717	0.165 P = 0.384	0.451 P = 0.012	-0.124 P = 0.514	0.232 P = 0.217
Colwell P mg/kg		1.000	0.278 P = 0.137	0.273 P = 0.144	0.870 P = <0.001	0.967 P = <0.001	0.175 P = 0.355	0.045 P = 0.813	0.180 P = 0.341	0.374 P = 0.042	-0.096 P = 0.614	0.169 P = 0.372
Oxalate Fe mg/kg			1.000	0.922 P = <0.001	0.645 P = <0.001	0.390 P = 0.033	0.895 P = <0.001	-0.658 P = <0.001	0.933 P = <0.001	0.703 P = <0.001	0.810 P = <0.001	-0.260 P = 0.165
Oxalate Al mg/kg				1.000	0.621 P = <0.001	0.397 P = 0.030	0.920 P = <0.001	-0.840 P = <0.001	0.969 P = <0.001	0.620 P = <0.001	0.876 P = <0.001	-0.211 P = 0.263
Ox P mg/kg					1.000	0.924 P = <0.001	0.546 P = 0.002	-0.256 P = 0.172	0.574 P = 0.001	0.617 P = <0.001	0.253 P = 0.174	-0.034 P = 0.858
Labile P mg/kg						1.000	0.315 P = 0.090	-0.075 P = 0.694	0.298 P = 0.110	0.393 P = 0.032	0.021 P = 0.912	0.003 P = 0.987
Organic C %							1.000	-0.696 P = <0.001	0.925 P = <0.001	0.736 P = <0.001	0.873 P = <0.001	-0.329 P = 0.076
pH (CaCl$_2$ 1:10)								1.000	-0.814 P = <0.001	-0.288 P = 0.123	-0.852 P = <0.001	0.184 P = 0.330
Pmax mg/kg									1.000	0.649 P = <0.001	0.889 P = <0.001	-0.239 P = 0.203
Slope of Freundlich										1.000	0.437 P = 0.016	-0.272 P = 0.146
Intercept of Freundlich											1.000	-0.568 P = 0.001
EPC$_0$ mg/L												1.000

4.2.3 Organic Carbon Analysis

The percent organic carbon content did vary between soils from 1.13% (average) in the D soils to the highest being 6.21% (average) in the RO soils (Table 4-2). Differences would be expected between the soils as they are all of different 'types' with different mineralogies (Table 4-1). This range is typical of many Australian soils and differences in carbon content would be expected due to differences in mineralogy, in particular the protective effect of clay (Spain *et al.,* 1983).

Within the soil groups the organic carbon results were fairly uniform with only small variations. Small variations within the soils would be expected due to natural discrepancies in the soil matrix (Table 4-2).

A good correlation was observed between organic carbon (%) and oxalate extractable Fe (P <0.01) and oxalate extractable Al (P <0.01) (Table 4-3). This may be due to the relationship between organic compounds and Fe and Al oxyhydroxides which bind to form humic complexes (Nguyen and Sukias, 2002).

 A significant correlation was observed between percentage organic carbon and the slope and intercept of the Freundlich curves (P <0.01 respectively) (Table 4-3). The Pmax was also well correlated to organic carbon (P <0.01) (Table 4-3). This illustrates the impact that organic matter has on P sorption.

4.2.4 Oxalate Extractable Iron and Aluminium

The oxalate extractable Fe, Al and P results were well correlated (P <0.01 respectively) (Table 4-3) as would be expected as they are all extracted by the

same method and as oxalate extractable P is a measure of the P bound to poorly crystalline Fe and Al oxyhydroxides which are the species extracted in the ammonium oxalate extractable procedure (Rayment and Lyons, 2011). The majority of the soils (excepting FL and D) contain the minerals gibbsite and goethite (Fe and Al oxyhydroxide minerals) (Table 4-1). Thus, the concentration of Fe and Al oxyhydroxides found varied among the soil types (Table 4-2). The fact that higher oxalate extractable Al was found in the FL soil than the KA soil (Table 4-2) is unexpected as the FL soil contains no gibbsite or goethite (Table 4-1). The Flaxley soil does have an orthoclase component that the KA soil does not, however the soil type with the highest orthoclase component (D) (Table 4-1) was found to have the least oxalate extractable Al values (Table 4-2). Perhaps this is an area which may need further investigation.

A strong correlation was observed between labile P and oxalate extractable Fe and Al ($P < 0.05$ respectively) (Table 4-3). This coupled with the fact that both Fe and Al oxalate extractable variables were very well correlated with the P_{max} of the soils calculated from the Langmuir equations ($P < 0.01$ respectively) and the slopes and intercepts of the Freundlich plots (both Fe and Al $P < 0.01$ respectively) (Table 4-3). The relationship between P sorption and Fe and Al oxyhydroxides has been well documented in previous research (as discussed in Section 2.2.2) and is another reason why oxalate extractable Fe and Al are popular tests commonly used in P sorption experiments (McDowell and Sharpley, 2001). The Fe and Al oxalate extractable methods are also less labour intensive in the determination of P sorption than the construction of P sorption isotherms and so can be a good quick alternative (Janardhanan and Daroub, 2010).

Previous P additions appear to have had no impact on either the Fe or Al oxyhydroxide content of the soils with no correlation evident (Table 4-3).

4.2.5 Soil Phosphorus Tests; Colwell, Labile and Oxalate Extractable

The previously added P (as the fertiliser TSP) had an impact on Colwell P. There was a good correlation observed between the Colwell P results and the presorbed P (P <0.01) (Table 4-3). Within all soil types, Colwell P was observed to increase as fertiliser treatments increased (Figure 4-1). This is expected as fetilisers are usually applied to soils in order to increase crop yields, thus the P needs to be in a bioavailable from and Colwell P is a measure of readily available P relating to crop/pasture growth (Rayment and Lyons, 2011). This is further illustrated through the good correlation between Colwell P and Labile P (P <0.01) as would be expected as they are both a measure of 'available' P (Table 4-3).

Previously added P and Labile P correlate very well (P <0.01) (Table 4-3) and the curves of Colwell P and Labile P plotted against the previously added P fertiliser are almost identical (Figure 4-1). There was a slight difference observed between some of the soil types with some results higher than others (Figure 4-1). For example, the RO, MA and MO curves are more elongated with higher labile and fertiliser P than that for D which exhibits a much lower curve and values (Figure 4-1). The RO, MA and MO soils also happen to be the more highly sorbing soils whereas D is the lowest sorbing (Figure 4-5; Appendix I and as discussed further in Section 4.2.6). Across all soils as fertilser treatments increased so did labile P (Figure 4-1, Table 4-2). This parallels the results for Colwell P, for the same reasons as noted previously; fertiliser 'creates' an

Figure 4-1: The relationship between differing phosphorus fertiliser additions to six Australian soils and the the phosphorus extraction methods; **(A)** Colwell P (mg/kg) **(B)** labile P (mg/kg) and **(C)** oxalate extractable P (mg/kg). Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson

available source of P in the soil to which it is added. In research carried out by Zhang *et al.,* (2004) - they found that residual P from fertilisers converted rapidly into labile P which is less tightly bound to the soil particles, thus it is at a greater risk of desorbing and being transported into water systems. Labile P is an organic component of the solid phase of soil P that rapidly equilibrates with soil solution or runoff and surface water; conversely, less available forms of P are slowly released into solution (Sims and Pierzynski, 2005). The concentration of labile P in a soil will generally slowly decrease (depending on buffering conditions) if the soil is not replenished with P, (for example, with fertiliser), or if less than optimal amounts of fertiliser are used (Rayment and Lyons, 2011). Phosphorus loss occurs via crop removal and labile P can decrease to the extent that the soil may no longer be able to support abundant plant life. Therefore, for a given soil the more abundant the labile P the longer the soil can maintain plant life (Sims and Pierzynski, 2005).

Oxalate extractable P and previously added P exhibited a very clear correlation (P <0.01) (Table 4-3). Oxalate extractable P increased as fertiliser amendment rates increased (Table 4-2, Figure 4-1). This illustrates the idea that a portion of the fertiliser P was in the form of oxalate extractable P once in the soil matrix.

Colwell P and oxalate extractable P exhibited a good correlation (P <0.01) (Table 4-3). Graphing of oxalate extractable P results against Colwell P showed a generally increasing trend in all soil types between an increase in Colwell P and an increase in oxalate extractable P (Figure 4-2). The RO soil exhibited the highest P affinity curve with the highest values in each variable (Figure 4-2).

Oxalate extractable P V Colwell P

Figure 4-2: The relationship between Colwell P (mg/kg) and oxalate extractable P (mg/kg) in six Australian soils with varying phosphorus fertiliser amendment rates. Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson.

The D soils exhibited the lowest increase in each variable and thus the 'shallowest' curve and lowest values (Figure 4-2).

A clear relationship was observed between oxalate extractable P and labile P ($P < 0.01$) (Table 4-3, Figure 4-3). This indicates both measurements were an appropriate test for P estimation in these soils. A general trend of increasing labile P was seen as oxalate extractable P increased over the range of fertiliser treatments for all six soils (Figure 4-3). Thus, Increases in the fertiliser concentration of the soil had an impact on both variables (Figure 4-3, Table 4-2; Table 4-3) as discussed previously. Even though a good correlation was observed between these two variables, oxalate extractable P is a much more widely used and accepted estimation of total P sorbed than labile P (Fransson, 2001; Agudelo *et al.*, 2011; Turner and Engelbrecht, 2011).

Figure 4-3: Increasing trend between labile P (mg/kg) and oxalate extractable P (mg/kg) over six Australian soils with varying amounts of P fertiliser additions. Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson.

Labile P measurement only represents a fraction of the total P of the soil, (the bioavailable 'loosely' bound P) whilst oxalate extractable P measures that P associated with the poorly crystalline Fe and Al oxyhydroxides; a very reliable soil P estimation (Fransson, 2001; Agudelo *et al.*, 2011; Turner and Engelbrecht, 2011). As this relationship between oxalate extractable P and labile P can be observed across the varying soil mineralogies and P treatments it may indicate a relationship common across differing soil matrices with implications that oxalate extractable P may be an effective surrogate for the technically more difficult measure of labile P.

A graph of oxalate extractable P vs oxalate extractable Al shows an increase in oxalate extractable P as the P fertiliser concentration increases (Figure 4-4, Table 4-2).

Oxalate extractable P V Oxalate extractable Al

Figure 4-4: Oxalate extractable P (mg/kg) against oxalate extractable Al (mg/kg) over a range of phosphorus fertiliser amendment rates for six Australian soils. Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson.

 It is also clear that the higher sorbing soils (RO and MA) have a higher oxalate extractable Al and oxalate extractable P value than those lower sorbing soils (such as D and KA) (Figure 4-4, Table 4-2). This is expected as previous research has confirmed that oxalate extractable Al is a good measure of P sorption capacity of a soil (McDowell and Condron, 2000; McDowell and Sharpley, 2001).

The slope of the Freundlich curve and oxalate extractable P exhibited a significant correlation (P <0.01) (Table 4-3). This relationship serves to further the idea that oxalate extractable P is a valid method of determining P in Australian soils.

4.2.6 Phosphorus Sorption Analysis

Sorption curves were prepared for each soil. The effect that pre-sorbed P (predominantly from TSP fertiliser) had is obvious when sorption curves for each soil type are represented on one graph (Figure 4-5; Appendix I). The previously added P has had an impact on new additions otherwise all curves would be identical to the 0 mg/kg previously added P sample (the same concentrations of P standards have been added to each soil thus previously added P is the only variable between soils of the one type) (Figure 4-5; Appendix I). Sorption curves of a particular soil type exhibit the same shape it is the 'position' that they occupy relative to each other which is different and which is dependent on the amount of previously added P (Figure 4-5; Appendix I). This indicates that for a particular soil type the sorption curve is specific to that soil and it is the pre sorbed P which is the variable factor. This phenomenon has been observed in previous research by Beckwith (1965). In most cases the 0 mg P/kg fertilised soil occupied the highest position on the graph indicating it was the highest sorbing, followed by the smallest addition of previous P and the highest fertiliser rate being the lowest curve on the graph; the least sorbing (Figure 4-5; Appendix I). Only MO soils showed that the curve for 0 mg/kg previously added P was not the most intense of the soil group, and was actually the second most intense (Appendix I). The effect of pre-sorbed P has been described as very important and must be taken into account when undertaking soil P sorption experiments as it can represent a significant proportion of the total P content of the soil (Bache and Williams, 1971; Condron and Newman, 2011). These results coupled with the knowledge gained from previous research suggest that there is a 'residual' effect on all soils from the previously added P

(A) RO sorption curve

+ 0 mg P/kg (RO-1)   ○ 79 mg P/kg (RO-3)
□ 306 mg P/kg (RO-6)   ✕ 1038 mg P/kg (RO-10)
△ 2158 mg P/kg (RO-15)

(B) D sorption curve

+ 0 mg P/kg (D-2)   ○ 1098 mg P/kg (D-4)
□ 81 mg P/kg (D-6)   ✕ 234 mg P/kg (D-8)
△ 610 mg P/kg (D-11)

Figure 4-5: Sorption curves generated from phosphorus soil sorption experiments. Pictured here are the highest and lowest sorbing soils. **(A)** The highest sorbing soil Robertson (RO), NSW, Australia. **(B)** The lowest sorbing soil Richmond (D), NSW, Australia.

and the greater the amount of pre-sorbed P the lower the sorption of subsequent applications; thus the sorption of P is not in direct proportion to the increasing amount of P added to the soil (Figure 4-5; Appendix I) (Bache and Williams, 1971; Sharpley *et al.,* 1984; McDowell and Sharpley, 2001; Ahmed *et al.,* 2008; Condron and Newman, 2011).

A plateauing of the sorption curves was seen in all soil types; depicting soils reaching their P threshold concentration (or sorption maxima) (Figure 4-5; Appendix I). This is a well known phenomenon; P sorption is not linear and there is a level at which further additions of P will not be sorbed (as soils do not have unlimited binding sites available for P) and will have no further impact on the 'secondary' effects caused by P sorption (Barrow, 2002; Ahmed *et al.,* 2008).

The RO soils were found to be the highest sorbing of all the soils. This can be discerned via the sorption curves as only RO-15 (the soil with the greatest P fertiliser added) shows an 'extended plateau' (Figure 4-5). Another highly sorbing soil (MA) also exhibited the same characteristic (Appendix I). The RO soils were found to be the highest sorbing and also had the least amount of quartz as well as larger amounts of other clay and mineral components as discussed in Section 4.2.1 (Table 4-1). Other soils with higher contents of kaolin, goethite, gibbsite and illite were also some of the more highly sorbing soils (including MA and MO) (Table 4-1; Appendix I). Conversely FL and D do not contain any goethite or gibbsite and were the two lowest sorbing soils (Table 4-1; Figure 4-5; Appendix I).

Negative sorption values were observed in the 0 mg/kg new P addition in all soils. This indicates desorption of P from the soil (Figure 4-5; Appendix I) an occurrence which has been documented in previous P sorption studies (Barrow, 2002). This desorption in a sample with no P added indicates there is already some P present in the soil before additions are made.

Some crossing of sorption curves at low concentrations (in the linear portion of the curves) has occurred in MO and KA soils (Appendix I). This has been reported by Bache and Williams (1971) in which it is described as being a function of differing pre-sorbed P values.

Soils with steep sorption curves (such as RO and MA soils) (Figure 4-5; Appendix I) indicate these soils are highly sorbing and are usually characterised by being strongly buffered when it comes to 'releasing' P or making it available (Beckwith, 1965). The opposite is true for soils with more 'gradual' curves (such as, the D soils) (Figure 4-5).

The low sorption capacity of the D soils is illustrated in sample D-4 (which has the highest previous P additions) with all of points of the sorption curve under the base line; this indicates desorption for all points of that soil (Figure 4-5). Perhaps use of a lower concentration P standard (for the new P additions) may have given a better representation of the sorption characteristics of this soil. The mineralogy of the D soils plays a huge role in the low sorption capacity of the soil (as discussed in Section 4.2.1).

4.2.6.1 Equilibrium Phosphorus Concentration (EPC_0)

The EPC_0 values were calculated from the equation of the line of best fit (fitted by the computer program Numbers) for each of the sorption curves (Appendix II). Most of the EPC_0 values were very low and usually quite similar between samples of a particular soil type with small differences probably relating to differences between pre-sorbed P concentration (Table 4-4). The EPC_0 and intercept of the Freundlich sorption model gave a very good correlation (P <0.01) (Table 4-3) which indicates the Freundlich has modelled the P sorption of these soils appropriately. There are some high EPC_0 values in the D soil set especially with (D-4) as this soil only exhibited desorption therefore its EPC_0 value is much higher than others (Table 4-4). As discussed in Section 2.1 soils with a high EPC_0 value have a greater potential to release P (Vaananen *et al.,* 2008). This is due to their mineralogical composition which is exhibited in the D soils which have a lack of P-binding minerals such as goethite and gibbsite (Table 4-1).

4.2.7 Langmuir Sorption Curves

All of the soils in this project conformed well to either the Freundlich or Langmuir sorption models, or both. The soil data fit well to the linearised Langmuir equation (equation [1] Section 2.3.1) and straight lines with R^2 values between 0.433 (D-4) and 0.998 (FL-12) were produced (Figure 4-6; Appendix III).

The point corresponding to 0 newly added P usually fell below the base line equating to desorption which is not allowed for in the Langmuir model; due to this, the R^2 values quoted are for lines with the first point omitted (Campbell and

Table 4-4: Parameters derived from the phosphorus sorption curves, Langmuir and Freundlich soil sorption models of six Australian soils. Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson

Soil	Tray No.	Pmax (mg/kg)	Slope of Freundlich plots	Intercept of Freundlich plots	EPC_0 (mg/L)
D	2	91	0.2837	1.4403	0.406
D	4	-6.39	-	-	177
D	6	51.8	0.2562	1.2291	0.433
D	8	28.6	0.2112	0.9964	1.96
D	11	11.3	0.2188	0.64	13.5
KA	1	233	0.3782	1.7292	0.353
KA	5	250	0.348	1.7357	0.295
KA	8	222	0.3914	1.6431	0.782
KA	11	313	0.7067	1.1341	1.98
KA	15	294	0.545	1.3018	2.14
FL	2	303	0.4121	1.7593	0.264
FL	4	313	0.3922	1.7654	0.583
FL	9	313	0.4136	1.7176	0.589
FL	12	263	0.5521	1.3328	1.86
FL	15	345	0.7029	1.0691	3.08
MO	2	556	0.4229	2.1324	0.178
MO	5	500	0.6405	1.5002	0.561
MO	6	625	0.4252	2.1313	0.238
MO	9	625	0.476	1.9916	0.456
MO	11	588	0.5119	1.8545	0.614
MA	1	909	0.4444	2.629	0.049
MA	3	909	0.408	2.5753	0.039
MA	7	909	0.4443	2.5112	0.078
MA	11	909	0.4875	2.334	0.141
MA	15	714	0.6097	1.8499	0.872
RO	1	1429	0.6316	3.0685	0.034
RO	3	1667	0.7509	3.0518	0.048
RO	6	2000	0.754	2.9523	0.073
RO	10	1667	0.5802	2.7756	0.084
RO	15	1667	0.6006	2.5076	0.220

Davies, 1995). Desorption on the first point was found in all soil types in this study (Figure 4-6; Appendix III) and has been observed in other research (Barrow, 2002).

The D soils were the lowest sorbing of the soils tested and the Langmuir model fits this soil slightly better than the Freundlich, except for sample D-4 due to the high level of desorption experienced (Appendices IV and V). When a soil fits one model better than another, it means that the assumptions inherent in that model (in this case the Freundlich) are less valid for that soil (Campbell and Davies, 1995). In many instances the single term Langmuir equation can give a good fit over a narrow concentration range although the fitted sorption maximum is not a true indication of saturation (Lewis and McGechan, 2002).

Ahmed *et al.*, (2008) found the Langmuir equation gave a very good fit of their Camden soil, better than the Freundlich. This was also the case for all Camden soil samples in this research except for KA-15 (the soil with the highest fertiliser amendment rate) (Appendices IV and V).

4.2.7.1 Phosphorus sorption maxima (P_{max})

The data indicates that the P_{max} remained relatively constant over each soil type (as expected) - the pre-sorbed P did not seem to have any impact upon this variable (Table 4-4). The P_{max} increased slightly in some soils with an increase in P added (this was seen in KA and FL soils) (Figure 4-7). This is mirrored in results obtained by Zou *et al.* (2011) who found that P_{max} increased in rice paddy soils over time with increased use until the 700 year mark when they began to decline. The P_{max} values correlate quite well with the intercept (P <0.01) and slope of the Freundlich (P <0.01) plots which may serve as a

Figure 4-6: Two Langmuir sorption curves for phosphorus additions to soils previously treated with triple superphosphate fertiliser. **(A)** Flaxley (FL) soil from SA, the best fitting Langmuir sorption model of the soils tested (previous fertiliser amendment rate (658 mg P/kg). **(B)** Richmond (D), NSW soil, the worst fit of the Langmuir sorption model of the soils tested (previous fertiliser amendment rate (1098 mg P/kg).

Pmax V Phosphorus Fertiliser Additions

Figure 4-7: The P_{max} of the six Australian soils studied stayed relatively constant over a range of phosphorus fertiliser additions. Where D - Richmond; KA - Camden; FL - Flaxley; MO - Glenmore; MA - Bowral; RO - Robertson

confirmation of the results (Table 4-3). Ahmed *et al.* (2008) found the P_{max} of their Camden soil to be 222 μg/g which is comparable with results obtained in the study (Table 4-4). The results found in this study (Table 4-3) are in accordance with results found by Janardhanan and Daroub (2010) where oxalate extractable Fe, Al and pH values were also found to correlate well with P_{max} values for soils in Southern Florida.

4.2.8 Freundlich Sorption Curves

All soil data were fitted to the Freundlich model of log x (P adsorbed/kg) vs log c (equilibrium P concentration mg P/L). Most of the soils fitted well to the Freundlich equation exhibiting relatively straight lines with R² values between 0.558 (D-8) and 0.967 (FL-2) (Figure 4-8; Appendix IV).

The relatively high R² values obtained coupled with the good correlation between the Freundlich intercept and EPC_0 (as discussed in Section 4.2.6.1)

Figure 4-8: Two Freundlich sorption curves for phosphorus additions to soils previously treated with triple superphosphate fertiliser. **(A)** Flaxley (FL) soil from SA, the best fitting Freundlich sorption model of the soils tested (previous fertiliser amendment rate (0 mg P/kg). **(B)** Richmond (D), NSW soil, the worst fit of the Freundlich sorption model of the soils tested (previous fertiliser amendment rate (234 mg P/L).
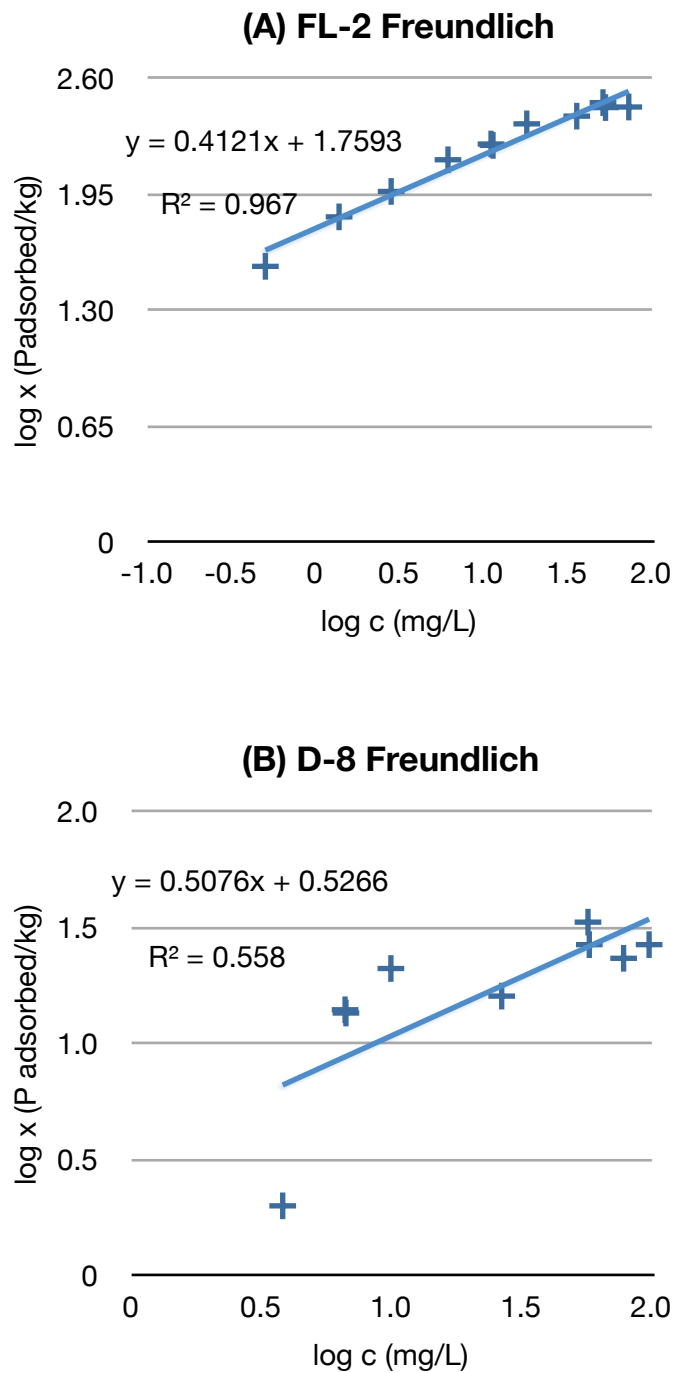
indicate that the Freundlich isotherm model describes the characteristics of the P sorption of the soils well. All R² values quoted are from curves with the first point omitted; due to desorption taking place when no new P was added a negative value was obtained and thus cannot have a log applied. The D soils were the only exception to this; due to low sorption by this soil and an increased level of desorption in the soils with higher previously added P, log/log curves were either not able to be produced (as in the case of D-4) or were ill fitted for the soil (D-8 and D-11) (Figure 4-8; Appendix IV)

4.2.9 Comparisons Between Langmuir and Freundlich Sorption Models

Even though both Freundlich and Langmuir isotherms are commonly used to depict P sorption data, it is also commonly accepted that these models do not always accurately describe the quantity/intensity relationship (Gunary, 1970; Bache and Williams, 1971; Hinz, 2001).

Due to issues inherent in these sorption models, much research has been done in an attempt to improve them and make them more applicable to soils. Mead (1981) found that the Langmuir equation was the least suitable fit for their soil data, (of 38 northern NSW soils) as it underestimated sorption at both extremes of the curve, overestimated the intermediate points and gave an unsatisfactory intercept and high standard deviation. To amend the Langmuir equation in order to better describe soil data some success has been had with the 'two-component' Langmuir model (or Langmuir II); however this equation is more time consuming than the original in that it requires many more data points and is quite a bit more elaborate (Fitter and Sutton, 1975). Mead (1981) found the Langmuir II gave the best fit for their NSW soils but found the coefficients were

very similar to those found with the Freundlich; thus the conclusion was reached that the Freundlich was the best isotherm to use as it not only provided a good fit to the data but was also simple and therefore very good for commercial testing.

Fitter and Sutton (1975) added another term to the Freundlich equation ('a') which represented the P which must be removed to reduce the concentration of the soil to 0 (to account for any pre-sorbed P). The original Freundlich isotherm often produces a curve and is only linear over a limited concentration range. By adding their 'a' term, Fitter and Sutton (1975) found they could reduce the deviations especially at the lower ends of the concentration range (and found it was linear over 0.1-100 μm P which is the concentration most relevant to studies of plant uptake of P). Conventional curves plot the laboratory added P sorbed only and do not take into account the pre sorbed P which can make comparisons between soils less meaningful (Fitter and Sutton , 1975). Mead (1981) found that out of three common sorption models (Freundlich, Langmuir and Temkin) that the Freundlich fitted the data best when an estimation of the pre-sorbed P was included. This was not found to be the case in this research as the Langmuir was found to fit the soils best. The addition of either labile or Colwell P values as estimates of pre-sorbed P did not improve the linearity of the Freundlich or Langmuir plots for any of the soils. A preliminary evaluation not presented here due to time restraints indicates that oxalate extractable P, as an estimate of pre-sorbed P, may be appropriate for the soils tested as the values obtained for oxalate extractable P are much larger than the Colwell or labile P measures (which could indicate why they failed to improve the fit of the models).

4.2.10 Comments on Factors Impacting Phosphorus Sorption

Previously added P fertiliser treatments had an obvious impact on the behaviour of new P additions in that the higher the amount of fertiliser applied, the less new P was sorbed. This indicates previously added P has a residual effect and can accumulate in the soil. Thus, the same amount of P will not be required to be applied each year to achieve the required available P for crop optimisation. What complicates the matter is the individual characteristics of the soil the P is to be applied to coupled with the location and use of the land. Thus, researchers suggest a holistic approach to eutrophication mitigation. This can be achieved via a range of management strategies including:

- lowering P fertiliser and manure application rates to directly meet the needs of the crops, animals and land needs,

- removing or redistributing animal wastes over the land area,

- more efficient irrigation methods,

- control of urban runoff through better sewerage systems,

- retaining wetland and 'buffer' vegetation as well as mitigating erosion especially around water catchments (Carpenter *et al.,* 1998; Nguyen and Sukias, 2002; Tilman *et al.,* 2002; Toor *et al.,* 2004).

The removal of animal manures from agricultural land may not only serve to limit P movement into waterways but excess P within the manure may be able to be extracted and reused (Gilbert, 2009). Researchers also affirm the importance of developing a test to define the P threshold value for soils but often comment that this is a difficult task with varying soil mineralogy and

physico-chemical parameters and the complexity of the P source (Carpenter *et al.,* 1998; Sims and Pierzynski, 2005).

CHAPTER 5 Conclusions and Recommendations:

This research has completed an extensive body of work on P in soils previously treated with P. A number of conclusions and recommendations forthcoming in this work as presented in this chapter.

5.1 Conclusions

• Previous treatment of soils with fertiliser clearly has an effect on subsequent additions of P (even after two years). A residual effect means that soils cannot sorb as much P. The larger the previous P treatment the less 'new' P can be sorbed. This shows that depending on soil chemical characteristics P can remain in (and still impact upon) the soil for long periods of time.

• Some soil characteristics were affected by previous P treatments. The pH was raised slightly, labile, Colwell and oxalate extractable P all increased with increasing P fertiliser amendment rates.

• P sorption was affected by chemical variables (pH, organic carbon content, concentration of reactive species, such as, Fe and Al oxyhydroxides and mineralogy). These variables change the 'form' of the P present in the soil matrix and its ability to sorb or solubilise.

• Although there was insufficient time to develop a mathematical model the results obtained in this research will be valuable in the synthesis of a new more 'complete' model especially for P sorption in soils. Some additional research/experimentation will be needed (for example soil pH buffering capacity), for a functional and thorough model to be developed.

5.2 Recommendations:

There has been much research undertaken in the past that explores the behaviour of P in soils and how to minimise P leaching into waterways; however, results are hard to compare between different countries, different sites and different soils due to the complex nature of the soil matrix and the many factors, (physical, chemical and biological), that combine to influence the behaviour of P in soils. Although only six soils are used in this study they have a wide range of properties and P histories (and are well characterised). Consequently, the results have the potential to contribute to a deeper understanding of P sorption by soils. The information obtained will be a valuable contribution towards the development of predictive models to ascertain the risk of P pollution which is a crucial global environmental issue. Further research is needed to develop a successful model including soil pH buffering capacity. A model considering all of the factors detailed in this report (as well as some additional parameters that there was insufficient time to characterise) could lead to better management of P; decreasing wastage and P initiated eutrophication. A P sorption model specifically for P-soil interactions will also mean less wastage of an element which is non-renewable and provide positive economic impacts for agriculture.

Eutrophication caused by P is an important problem on a global scale, in order to make in-roads on this issue, research must start at the local level. Firstly, determining tests and factors which affect P sorption and retention across different soil types encompassing relationships between the physical, chemical and biological aspects of the soil and its environment, then the development of a model based on these relationships in order to determine P threshold values

in soils of a variety of types and locations. Larger scale studies undertaken in different climatic zones in different countries and on lands of differing uses over a longer term (perhaps 10 years or more) would greatly further the knowledge in this field of research and help create a more accurate model.

Education for agriculturalists on why P management is so important and the benefits it can have for them (both monetary and environmental) is an important issue to address.

Phosphorus management is still a critical issue in agriculture (for reasons noted earlier in the thesis). While this study has furthered our knowledge on this issue, there is still more to be done in order to markedly improve P management and ensure effective and efficient use of the limited P resources available globally.

CHAPTER 6 References

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APPENDIX I

Soil P sorption curves

KA sorption curve

+ 0 mg P/kg (KA-1)
○ 90 mg P/kg (KA-5)
□ 260 mg P/kg (KA-8)
× 599 mg P/kg (KA-11)
△ 1047 mg P/kg (KA-15)

FL sorption curve

+ 0 mg P/kg (FL-1)
○ 96 mg P/kg (FL-4)
□ 286 mg P/kg (FL-9)
× 658 mg P/kg (FL-12)
△ 1031 mg P/kg (FL-15)

MO sorption curves

+ 0 mg P/kg (MO-2)
○ 1248 mg P/kg (MO-5)
□ 71 mg P/kg (MO-6)
× 348 mg P/kg (MO-9)
△ 602 mg P/kg (M0-11)

MA sorption curve

+ 0 mg P/kg (MA-1)
○ 55 mg P/kg (MA-3)
□ 188 mg P/kg (MA-7)
× 604 mg P/kg (MA-11)
△ 1322 mg P/kg (MA-15)

APPENDIX II

Equations for line of best fit for each sorption curve (used to calculate the EPC_0)

Soil - Tray No.	Equation	Soil - Tray No.	Equation
D-2	y=17.197ln(x)+15.517	KA-1	y=40.634ln(x)+42.347
D-4	y=5.9045ln(x)-30.562	KA-5	y=39.207ln(x)+47.861
D-6	y=10.007ln(x)+8.3802	KA-8	y=47.689ln(x)+11.738
D-8	y=7.8738ln(x)-5.8305	KA-11	y=57.672ln(x)-39.369
D-11	y=8.701ln(x)-22.627	KA-15	y=51.805ln(x)-39.319
FL-2	y=49.243ln(x)+65.675	RO-1	y=281.1ln(x)+954.53
FL-4	y=56.891ln(x)+30.706	RO-3	y=352.56ln(x)+1074.6
FL-9	y=56.266ln(x)+29.827	RO-6	y=366.97ln(x)+960.25
FL-12	y=53.974ln(x)-33.594	RO-10	y=299.32ln(x)+741.1
FL-15	y=65.136ln(x)-73.35	RO-15	y=307.06ln(x)+464.87
MA-1	y=162.79ln(x)-492.14	MO-2	y=93.263ln(x)+160.99
MA-3	y=142.27ln(x)+461.09	MO-5	y=105.01ln(x)-60.658
MA-7	y=158.15ln(x)+403.36	MO-6	y=106.53ln(x)+153.15
MA-11	y=151.23ln(x)+295.94	MO-9	y=109.29ln(x)+85.74
MA-15	y=142.55ln(x)+19.51	MO-11	y=102.8ln(x)+50.06

APPENDIX III - LANGMUIR CURVES

D - Richmond, NSW Langmuir curves

D-2 Langmuir

$y = 0.011x + 0.0638$
$R^2 = 0.964$

c/x (kg/L) vs c (mg/L)

D-6 Langmuir

$y = 0.0193x + 0.1045$
$R^2 = 0.9482$

c/x (kg/L) vs c (mg/L)

D-8 Langmuir

$y = 0.0297x + 0.6267$
$R^2 = 0.7823$

c/x (kg/L) vs c (mg/L)

D-11 Langmuir

$y = 0.0918x + 0.017$
$R^2 = 0.5583$

c/x (kg/L) vs c (mg/L)

KA - Camden, NSW Langmuir curves

KA-1 Langmuir

$y = 0.0041x + 0.0259$
$R^2 = 0.9563$

KA-5 Langmuir

$y = 0.004x + 0.0335$
$R^2 = 0.9924$

KA-8 Langmuir

$y = 0.0041x + 0.0428$
$R^2 = 0.9802$

KA-11 Langmuir

$y = 0.0028x + 0.1149$
$R^2 = 0.7866$

KA-15 Langmuir

$y = 0.0082x + 0.0594$
$R^2 = 0.5837$

FL- Flaxley, SA Langmuir curves

FL-2 Langmuir

y = 0.0033x + 0.0217
R² = 0.9926

c/x (kg/L) vs c (mg/L)

FL-4 Langmuir

y = 0.0032x + 0.0299
R² = 0.9788

c/x (kg/L) vs c (mg/L)

FL-9 Langmuir

y = 0.0032x + 0.0321
R² = 0.9803

c/x (kg/L) vs c (mg/L)

FL-15 Langmuir

y = 0.0022x + 0.1674
R² = 0.5102

c/x (kg/L) vs c (mg/L)

MO - Glenmore, NSW Langmuir curves

MO-2 Langmuir

$y = 0.0018x + 0.0058$

$R^2 = 0.9952$

MO-5 Langmuir

$y = 0.0015x + 0.0572$

$R^2 = 0.7886$

MO-6 Langmuir

$y = 0.0016x + 0.0076$

$R^2 = 0.9841$

MO-9 Langmuir

$y = 0.0016x + 0.0129$

$R^2 = 0.9795$

MO-11 Langmuir

$y = 0.0017x + 0.0191$

$R^2 = 0.9815$

MA - Bowral, NSW Langmuir curves

MA-1 Langmuir

y = 0.0011x + 0.001
R² = 0.9361

MA-3 Langmuir

y = 0.0011x + 0.001
R² = 0.9835

MA-7 Langmuir

y = 0.0011x + 0.0015
R² = 0.971

MA-11 Langmuir

y = 0.0011x + 0.0031
R² = 0.9774

MA-15 Langmuir

y = 0.0013x + 0.0186
R² = 0.9253

RO - Robertson, NSW Langmuir curves

RO-1 Langmuir

$y = 0.0007x + 0.0003$

$R^2 = 0.9452$

RO-3 Langmuir

$y = 0.0004x + 0.0006$

$R^2 = 0.6178$

RO-6 Langmuir

$y = 0.0005x + 0.0007$

$R^2 = 0.6704$

RO-10 Langmuir

$y = 0.0005x + 0.001$

$R^2 = 0.7811$

RO-15 Langmuir

$y = 0.0006x + 0.0027$

$R^2 = 0.855$

APPENDIX IV - FREUNDLICH CURVES

D - Richmond, NSW Freundlich curves

D-2 Freundlich

y = 0.2837x + 1.4403

R² = 0.9172

(y-axis: log x (P adsorbed/kg), x-axis: log c (mg/L))

D-6 Fruendlich

y = 0.2565x + 1.2291

R² = 0.7678

(y-axis: log x (P adsorbed/kg)), x-axis: log c (mg/L))

D-11 Freundlich

y = 0.722x - 0.2282

R² = 0.6781

(y-axis: log x (P adsorbed/kg), x-axis: log c (mg/L))

KA - Camden, NSW Freundlich curves

KA-1 Freundlich

log x (P adsorbed/kg) vs log c (mg/L)

$y = 0.4265x + 1.6658$
$R^2 = 0.9286$

KA-5 Freundlich

log x (P adsorbed/kg) vs log c (mg/L)

$y = 0.4143x + 1.6428$
$R^2 = 0.9283$

KA-8 Freundlich

log x (P adsorbed/kg)) vs log c (mg/L)

$y = 0.4568x + 1.5515$
$R^2 = 0.9206$

KA-11 Freundlich

log x (P adsorbed/kg) vs log c (mg/L)

$y = 0.7881x + 1.0154$
$R^2 = 0.9374$

KA-15 Freundlich

log x (P adsorbed/kg)) vs log c (mg/L)

$y = 0.5023x + 1.2543$
$R^2 = 0.6548$

FL - Flaxley, SA Freundlich curves

FL-4 Freundlich

$y = 0.4622x + 1.6613$
$R^2 = 0.923$

log x (P adsorbed/kg)

log c (mg/L

FL-9 Freundlich

$y = 0.4758x + 1.6218$
$R^2 = 0.9471$

log x (P adsorbed/kg)

log c (mg/L)

FL-12 Freundlich

$y = 0.6677x + 1.1672$
$R^2 = 0.9075$

log x (P adsorbed/kg)

log c (mg/L)

FL-15 Freundlich

$y = 0.8342x + 0.8664$
$R^2 = 0.9136$

log x (P adsorbed/kg)

log c (mg/L)

MO - Glenmore, NSW Freundlich cur

MO-2 Freundlich

$y = 0.4792x + 2.0858$
$R^2 = 0.9176$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MO-5 Freundlich

$y = 0.7494x + 1.3474$
$R^2 = 0.9219$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MO-6 Freundlich

$y = 0.4922x + 2.0614$
$R^2 = 0.9294$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg))

MO-9 Freundlich

$y = 0.5845x + 1.8689$
$R^2 = 0.9449$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MO-11 Freundlich

$y = 0.5712x + 1.7809$
$R^2 = 0.9618$

x-axis: log c (mg P/L)
y-axis: log x (P adsorbed/kg)

MA - Bowral, NSW Freundlich curves

MA-1 Freundlich

$y = 0.5531x + 2.5757$

$R^2 = 0.803$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MA-3 Freundlich

$y = 0.4642x + 2.5559$

$R^2 = 0.9006$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MA-7 Freundlich

$y = 0.5102x + 2.4809$

$R^2 = 0.8488$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MA-11 Freundlich

$y = 0.5526x + 2.274$

$R^2 = 0.9156$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

MA-15 Freundlich

$y = 0.6867x + 1.7636$

$R^2 = 0.913$

x-axis: log c (mg/L)
y-axis: log x (P adsorbed/kg)

RO - Robertson, NSW Freundlich curves

RO-1 Freundlich

$y = 0.6251x + 2.9257$
$R^2 = 0.668$

log x (P adsorbed/kg)

log c (mg/L)

RO-3 Freundlich

$y = 0.7731x + 3.0102$
$R^2 = 0.8137$

log x (P adsorbed/kg)

log c (mg/L)

RO-6 Freundlich

$y = 0.7761x + 2.9097$
$R^2 = 0.8469$

log x (P adsorbed/kg))

log c (mg/L)

RO-10 Freundlich

$y = 0.6421x + 2.7491$
$R^2 = 0.8254$

log x (P adsorbed/kg))

log c (mg/L)

RO-15 Freundlich

$y = 0.6788x + 2.4503$
$R^2 = 0.8614$

log x (P adsorbed/kg))

log c (mg/L)