Department of Environment and Agriculture

Low water-soluble superphosphate fertiliser for pasture production in south-western Australia

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material, which has been accepted for the award of any other degree or diploma in any university.

Signature: ....
Rowan John Maddern

Date: ....

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ABSTRACT

The leaching of phosphorus fertiliser directly affects pasture growth and contributes to environmental damage. Single superphosphate fertiliser is the commonly used phosphorus fertiliser for pastures and is derived from chemically treating rock phosphate into relative proportions of monobasic, dibasic and tribasic calcium phosphate. Eighty-six per cent of single superphosphate is the water-soluble monobasic calcium phosphate, which is also the form most likely to leach in soils with low phosphorus retention. Manipulating the fertiliser manufacturing process allows the ratio of monobasic, dibasic and tribasic calcium phosphate to be varied within the fertiliser. By altering the proportion of monobasic calcium to dibasic calcium which dissolves at a slower rate, it is possible to reduce the rate at which phosphorus leaches, thereby increasing the likelihood to be accessed by the plant.

Using two customised fertilisers manufactured from rock phosphate and three pure phosphate forms, two experiments were undertaken to measure differences in phosphorus solubility, leaching and plant growth, one in hydroponic conditions and the other in leaching columns without plants. To remove the effect of soil reaction with phosphate, the experiments used perlite. The results showed that the two fertilisers and the forms of phosphate dissolve and leach at different rates and the rate is depended on its percentage of each phosphate form. There is no significant difference between the dry matter yield of clover or ryegrass grown with low water-soluble superphosphate or single superphosphate. This experiment concluded that as cumulative rainfall increases, the amount of dibasic calcium phosphate should be increased relative to monobasic calcium phosphate in phosphorus fertiliser. This change of chemistry will maintain pasture growth and reduce phosphorus leaching.

The second set of glasshouse and field experiments extending the hydroponic and leaching experiments involved the use of three soil types (light, medium, and heavy – PBI between 9 to 120) with two pasture species (clover and ryegrass) from the Swan Coastal Plain of Western Australia. This research determined if changing the chemical composition of phosphorus fertiliser will maintain plant growth while reducing phosphorus loss to leaching. Rainfall was simulated to 900 mm to mimic typical rainfall conditions in this region. The results demonstrated that reducing phosphate solubility of the low water-soluble superphosphate significantly reduces phosphorus leaching losses in all three soil types, with no significant difference in pasture dry matter yield. Leachate analysis confirms that, given the same amount of rainfall, as the soil’s ability to retain phosphorus increases, the amount of phosphorus leaching is reduced. The results also show that manipulating the chemistry of single superphosphate fertiliser will reduce solubility on lighter, sandy soil types and, with 900 mm of rainfall, can significantly increase plant phosphorus use efficiency and decrease leaching. This research recommends that the percentage of dibasic calcium phosphate in superphosphate fertiliser should be increased as the soil’s ability to retain applied phosphorus decreases.

This glasshouse research was then applied to two field trials over three years for a pasture grazing system. The two trial sites were soil collection sites for two of the soils types used in the glasshouse. The two fertilisers, single superphosphate and low water-soluble superphosphate were applied annually to the field experiment sites at 0, 5, 10, 15 and 25 kg/ha of phosphorus and the dry matter yield was measured. Results show that low water-soluble superphosphate does not reduce pasture dry matter yield at any applied rate and significantly reduces phosphorus leaching by 50%. The results indicate that a lesser soluble, modified phosphorus fertiliser maintains pasture dry matter yield and reduces phosphorus loss to leaching on a range of soils with different phosphorus buffering indexes and rainfall conditions. The research in this thesis was novel in that it found that the differences in solubility created from the customised fertiliser manufacture of superphosphate can be used to reduce phosphate loss in agricultural systems in Western Australia and has application on a global scale.

AWARDS RELATING TO THIS THESIS

Maddern, R, Smith, B, 2012. Wesfarmers Innovation Awards – Environmental category: Coast Phos. Melbourne, Vic.

Maddern, R, Smith, B, 2012. Fertiliser Industry Federation of Australia (Platypus) – Environmental Award: Hobart, TAS.

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SYMBOLS AND ABBREVIATIONS

ANOVA	Analysis of variance
DAA	Days after application
DAS	Day after sowing
DCP	Dibasic calcium phosphate
DMY	Dry matter yield
h	Hour
ha	Hectare
LWSSP	Low water-soluble superphosphate
MCP	Monobasic calcium phosphate
mm	Millimetres
NV	Neutralising value
OC	Organic carbon
P	Phosphorus
PBI	Phosphorus buffering index
SCP	Swan Coastal Plain
SSP	Single superphosphate
TCP	Tribasic calcium phosphate
WA	Western Australia

CHAPTER 1 GENERAL INTRODUCTION

With a world population of seven billion people in 2015 and projections of population growth to increase up to 50% within the next four decades, combined with an expected increase in living standards, there is a huge challenge to increase food production within this timeframe (Cohen 2003; Sutovsky *et al.* 2015). Consequently, there is an increased demand for inputs such as fertiliser to sustain higher agricultural production of which phosphorus (P) is a critical nutrient that underpins modern agricultural crop and pasture production (George *et al.* 2016). Phosphorus plays a critical role in the nutrition of all plants as it is an essential element that contributes in a wide array of physiological and biochemical processes (Vance *et al.* 2003). Modern inorganic phosphate fertilisers used in crop production is a non-renewable resource that is derived from rock phosphate (Cordell *et al.* 2009). The most pessimistic scenario is that rock phosphate reserves could be depleted in 30 to 40 years (Rengel and Zhang 2011). There is an increasing need to maintain or increase food production utilising current agricultural land while reducing environmental impacts from applied inorganic P fertiliser; this is the challenge that underpins this thesis.

1.1 Research problem

Soils have been formed by natural processes that have maintained a global system of biodiversity of life on land (Amundson *et al.* 2015). The ability of soil systems to maintain life on this planet is due to its inherent balance between nutrient inputs and outputs for plant growth. Humanity has exploited these soil resources for thousands of years, and this has allowed the evolution of the human species. The area and diversity in soil types and nutrients have allowed agriculture to expand with population growth and allows civilisation to relocate when soil nutrient natural reserves have been depleted. Knowledge of nutrient pathways has enabled the reinvigoration of depleted soils with the application of nutrients (fertilisers) to maintain or increase food production (Shen *et al.* 2011).

The introduction of P fertilisers on predominantly infertile soil types found in Australia has greatly improved crops and pasture production over the last 100 years (Henzell 2007). The Swan Coastal Plain (SCP) in the south-west of Western Australia is the geographical region where the Swan River traverses from east to west before terminating in the Indian Ocean (Cummings and Hardy 2000). The SCP is 30 km wide and bound by the Indian Ocean to the west, the Darling Scape Range to the east, Cape Naturaliste the south and the urban River to the north. It consists of mainly of infertile sandy soil that is currently being used for agriculture and supports the majority of the population of Western Australia. The SCP supports a mixture of farming and urban environments and is comprised of a mixture of soil types, ranging from heavy clays to light sandy soils, with the large majority being light sandy soils. Pasture production systems in reliable high winter rainfall areas with sandy soils, such as in the SCP require annual P application to maintain production (Weaver and Reed 1998; Gourley *et al.* 2012).

The main sources of P in these pasture production systems are derived from rock phosphate that is manufactured into fertilisers. The effective application of P is critical to maintain long-term sustainability of agriculture. Pasture production requires high water-soluble superphosphate fertiliser as only the water-soluble form of P is taken up by plants (McLaren *et al.* 2015a). High water-soluble single superphosphate fertilisers are commonly used for agriculture on the SCP, however applying high water-soluble single superphosphate (SSP) on lighter soil types with high rainfall as recommended by Hanson and Foster (2012) increases P leaching through the soil, which accumulates in rivers, wetland and estuaries. The transport of excessively high levels of P each year to the waterways when introduced in large quantities creates problems such as algal blooms as outlined by Hodgkin and Hamilton (1993), mal-odours, fish deaths and eutrophication issues as discussed by (Carpenter 2008).

For the Swan River, which is the main river on the SCP, Cahill (2009) estimates that 26 tonnes of total P enter the Swan River catchment annually. Numerical modelling conducted by Cahill (2009) indicates that 14 tonnes of total P is an acceptable load for this system. To meet the goal of reducing 12 tonnes of total P entering the Swan and Canning River systems by fertiliser application alone would require removal of 132 tonnes annually of SSP applied to the soils in this catchment. Farmers on the SCP require an average of 150 kg/ha of SSP applied annually for pasture production (Neuhaus (2010). To maintain pasture production, while reducing runoff into waterways would require a significant decrease in the use of SSP or removal of a large area of pasture out of production (McLaren *et al.* 2015b). The optimum outcome for both farmers and the environment is reducing the movement of P while maintaining pasture production. Hence strategies and technologies need to be developed that can maintain this balance between P input and outputs.

1.2 Research background

Single superphosphate fertiliser has been essential for pasture production systems in Australian soils with low levels of P (Henzell 2007). As shown in Figure 1.1, P in a pasture system undergoes a complex series of chemical and physical reactions within a cycle where inputs such as fertiliser are required to maintain production, and P is lost, changed or exported as agricultural commodities. As shown in Figure 1.1, pastures require soluble P for plant growth.

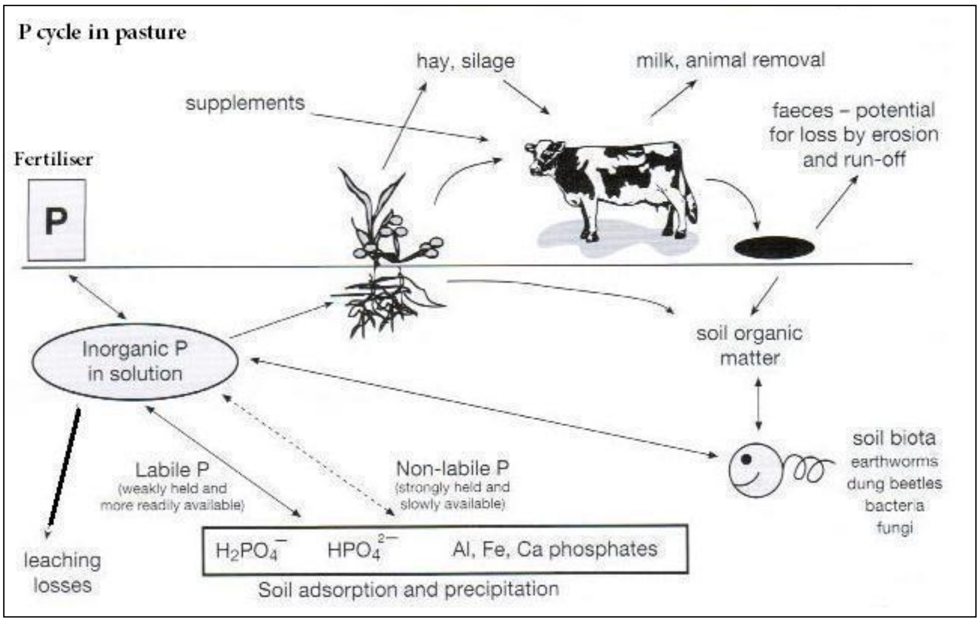


Figure 1.1 Phosphorus cycle in pastures (Price 2006). The movement of phosphorus within the agricultural system.

The light sandy soils and high winter rainfall combined with slow pasture growth in the colder months, as commonly experienced on the SCP production systems, frequently result in applied P leaching into waterways where it causes environmental damage (King *et al.* 2015). The high P leaching pressure and use of shallow rooted annual pasture species means that P applied before the break of the season may leach away before the spring months when it is needed. Thus a high percentage of applied P is being lost from the soil-plant system (Summers and Weaver 2008). Fertiliser should be applied to achieve the highest P use efficiency for any P fertiliser applied (McLaughlin *et al.* 2011; IPNI 2015).

In September 2006, the Minister for the Environment announced that high water-soluble superphosphate fertilisers will be phased out from environmentally sensitive areas of the south-west, Western Australia to reduce the environmental impact (Cox *et al.* 2007). The phase out was to occur over a four-year period, and if agriculture were to continue, a solution would have to be implemented. This phase out of high water-soluble superphosphate became known as the fertiliser action plan (Cox *et al.* 2007). At the time, there was no viable replacement strategy available for the replacement of SSP within this area. However, this phase-out plan was not implemented due to a change in Western Australian State Government and the problem of reducing eutrophication while maintaining pasture production systems remained.

Some methods can be used to reduce the loss of P leaching while maintaining pasture production systems including reducing the total rate of P applied in a single application and/or increasing the number of applications over the growing season (IPNI 2015). Multiple applications are not advisable as this is inefficient and it is not always possible to access the paddocks because of reduced trafficability during wetter months. There have been a number of attempts to find a solution to high P leaching (Yeates and Clarke 1993; Summers *et al.* 2001) which include applying increasing rates of bauxite residue as a soil amelioration to increase the soil capacity to hold onto P. The application of bauxite residue applied to sandy soil reduced P leaching and rates up to 1500 t/ha could be applied to the soils while maintaining a safe level of gamma radiation for human habitation (Summers *et al.* 1993a). Even within the required radiation safety standards for humans, large-scale adoption of bauxite residue did not occur (Summers *et al.* 2000). All existing methods to retain P in the soil are not effective as they will also limit pasture growth, increase the cost of production and/or have difficulty for public acceptance. Hence a novel approach is required.

1.3 The niche for novel

One possible solution to improve P fertiliser use is the manipulation of chemical properties of SSP to reduce P solubility. Fertiliser manufactured from rock phosphate such as SSP are comprised of three forms of phosphate (monobasic calcium, dibasic calcium and tribasic calcium) with the ratio of these dependent on the chemical reaction used (Agriculture 1964; Mclean and Wheeler 1964; Darlow 2009). An innovative approach is to change the chemistry of SSP by increasing the percentage of dibasic calcium phosphate (DCP) to reduce its solubility and allow P to be accessed by the plant before it could be lost to leaching. There has been limited work conducted globally, national and on the SCP on changing the chemistry of SSP and the proposed research will use current scientific methods to ensure its interoperability with current and past research. Please note that this PhD research was initiated during the government initiated phase out stage of the high soluble superphosphate fertiliser for the SCP.

1.4 Research objectives

The general research objectives are to evaluate the effectiveness of a low water-soluble superphosphate (LWSSP) fertiliser to maintain P within the plant rooting zone for a longer period within a pasture production system in south-west Western Australia. The effectiveness of LWSSP was determined through a series of comparative experiments with SSP fertiliser that involved hydroponics, glasshouse and the field. The specific research objectives are outlined below in Section 1.4.1.

1.4.1 Specific research objectives

The specific research objectives of this thesis are:

- To compare P solubility and leaching of LWSSP and SSP fertilisers and their chemical components for pasture production in hydroponic no-soil conditions.
- To compare P solubility, leaching and pasture production characteristics for LWSSP and SSP on three soil types soil under controlled glasshouse conditions.
- To compare LWSSP and SSP interactions on pasture production in field conditions by measuring dry matter yield, P plant tissue percentage and soil P levels.
- To develop a concept that models how LWSSP can fit into the pasture production system based on rainfall and P buffering index of the soil.

1.5 Thesis outline

This thesis is structured into seven chapters with chapter's four to six summarising scientific experiments with increasing complexity as explained in Figure 1.2. Chapter 7 is a general discussion and includes a proposed concept that is derived from this research.

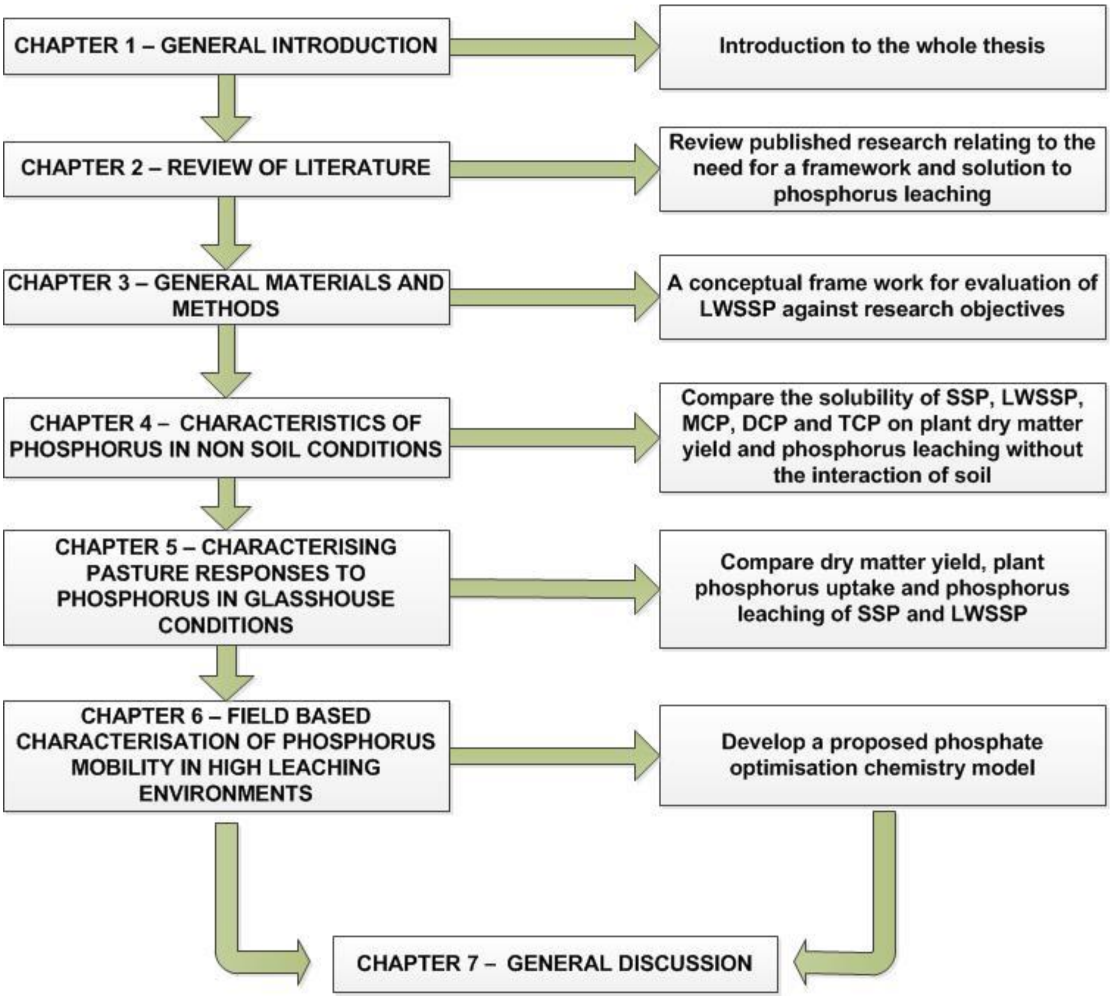


Figure 1.2 Thesis conceptual framework. This framework outlines the flow input, output and flow of this research and thesis. This thesis is divided into seven chapters comprised of three experiment chapters, each of which answers two of the specific research objectives. Single super phosphate (SSP), low water soluble super phosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP).

1.6 Research benefits

Benefits of this research arise from a greater understanding of the manufacture of P fertilisers and the fertiliser requirements on a pasture production system within high rainfall zone to minimise P loss to the environment. Very little research has been done that assesses the components of fertiliser and how these can be optimised for pasture production. This research evaluates fertiliser components and has global impact in fertiliser manufacture, design and application for pasture production systems. Further benefits for science is a broad overview of the customisation of phosphate forms within SSP to match pasture production systems, soil and rainfall conditions. There is considerable scope for the improvement and understanding of these areas and it is hoped that the benefits outlined here can be expanded upon into the future.

CHAPTER 2 REVIEW OF LITERATURE

2.1 Introduction

This review of the literature examines the pasture cycle for phosphorus (P) and components of the interacting systems as described in Figure 2.1. The areas that are examined include, soil Section 2.2, environment Section 2.3, plants Section 2.4, phosphorus Section 2.5 and management Section 2.6. The review of these subject areas will provide a broad overview of the pasture production on a global, national and specific situation found in a high rainfall high leaching agricultural environment such as the SCP of south-west Western Australia. The biggest environmental impact on the SCP environment is caused by leaching of applied soluble P fertilisers.

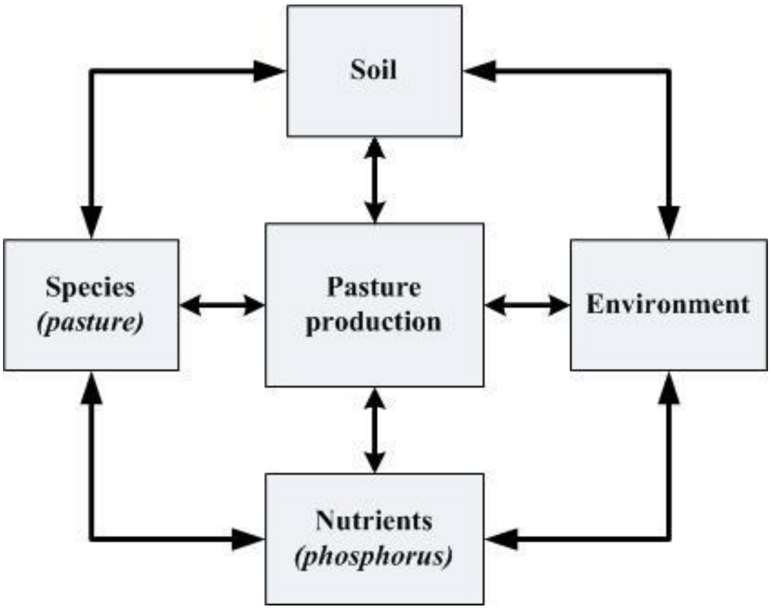


Figure 2.1 Flow diagram summarising the review of literature. The literature review will follow the flow of this diagram with the four topics each expanded upon and then methods for reduction of leaching for phosphorus fertilisers the last topic.

2.2 Soil

Soil is a granular structure that contains minerals and various elements organic compounds and organisms that together support plant life (Marzaioli *et al.* 2010). *“Soil structure can be described in terms of its grade or degree of structure, shape and size of aggregates, and stability of the aggregates. In agronomic terms, a `good' soil structure is one which shows the following attributes: optimal soil strength and aggregate stability, which offer resistance to structural degradation (capping/crusting, slaking and erosion, for example), optimal bulk density, which aids root development and contributes to other soil physical parameters such as water and air movement within the soil, optimal water holding capacity and rate of water infiltration. Unfortunately there is no ideal prescription for what is the best tilth”* (Sharpley *et al.* 2003).

Agricultural soils globally vary widely in their structure, chemical and physical properties however all soils require adequate nutrients and moisture for the production of pastures (Jobbágy and Jackson 2001). Physical factors can have a large influence on the availability of nutrients within soils such as bulk density, soil type, moisture, permeability, friability, location of nutrients in the profile and how tightly the nutrient is bound to the soil (Letey 1985; Schoenholtz *et al.* 2000). Chemical properties affect the availability of any present nutrients within the soil and while there could be adequate nutrients present they may not all be available to the plant. One of the major chemical constraints on nutrient availability in modern agricultural systems is pH (Chen and Barber 1990; Fageria and Stone 2006). The availability of different nutrients will change depending upon the pH level with elements such as aluminium becoming toxic to the plant at lower pH levels (Dong *et al.* 1999). Rainfall, soil moisture and permeability influences the growth of plants and affects the plants ability to extract nutrients from the soil and extended dry periods reducing nutrient availability (Oorschot *et al.* 1998). The lack of moisture will exacerbate nutrient deficiencies and the application of fertiliser to the plant is more critical in dryer conditions.

Soils sorption-desorption properties affects all nutrients, with the soil physical properties determining how this process takes place and the rate of nutrient release (Fox and Kamprath 1970; Huang *et al.* 2014). As the soil particle size decreases, the ability for the soil to retain nutrients increases (Moore 2004). The availability of different nutrients varies with soil type and conditions of which P is just one nutrient (Dawson and Hilton 2011). The quantity and availability of nutrients required for plant production will determine if there is a requirement for extra nutrition through fertilisation (Ezui *et al.* 2016).

Typical Australian soils are relativity low in natural nutrients critical for agricultural crop production, such as nitrogen (N), phosphorus (P), potassium (K), sulphur (S), and zinc (Zn) (Moore 2004; Tan *et al.* 2005). There is a large variation in the distribution of nutrients in Australia soils, particularly P, with less than 0.3 t/ha present in the top 30 cm from soils in the south-west of Western Australia. In comparison with the eastern states of Australia that have P levels generally about 1.5 t/ha of P within the top 30 cm.

Soil can be classified on soil properties such as texture and profile, which aids farmers globally to understand soil differences and to manage their farming systems for productivity. Soil classification systems vary across regions but are generally based on texture, topography, geological history, use and nutrient content (Baruck *et al.* 2016). Within Australia agricultural soils, there are 14 classifications or types of soil based on the Australia Soil Classification (ASC) system outline by Isbell (2016), which is discribed in the Appendix Section 9.2.1. The distributions of these soils are outlined in Figure 2.2 and show the variation of soil types present in Australia.

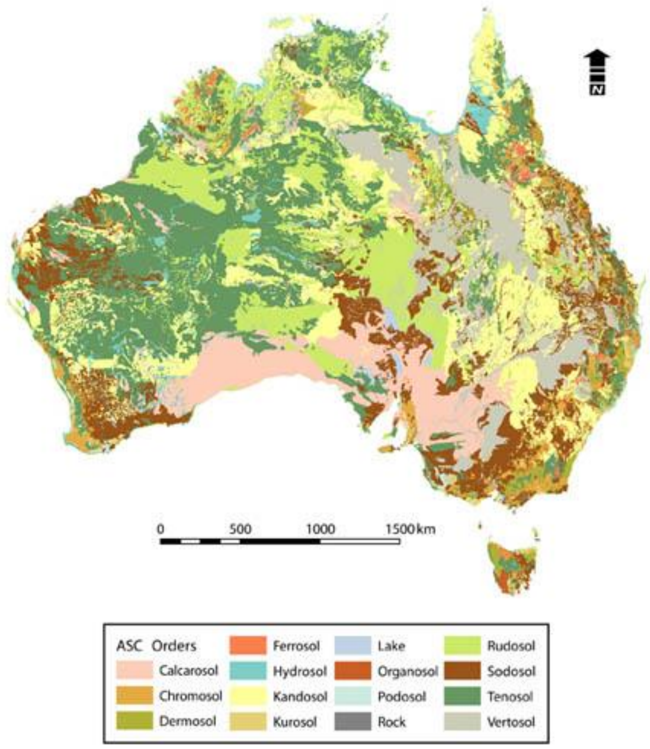


Figure 2.2 The distribution of Australian soil types (Ashton and McKenzie 2001).

The structure and type of soil has a significant effect on the availability of nutrients and moisture retention for plant growth. The structure of soil can change over time through natural and agricultural process, and this can influence the growth of pastures. Five key issues have been identified by Taylor *et al.* (2010) that cause loss of soil productivity; these are soil compaction, loss of soil organic matter, excessively high fertility levels, erosion risk, and the accumulation of contaminants. The structure of soil can change due to compaction of grazing livestocks that could reduce water penetration and nutrient availability (Greenwood *et al.* 1998).

The optimum soil type and structure for pasture production should include, a deep friable profile to allow easy of root penetration, good moisture holding capacity while not being water-logged, no physical or chemical barriers, adequate nutrients that are plant available and not tightly bound to the soil. Reduction of these factors can limit plant growth, but some can be overcome through management (Pulido *et al.* 2016). It is considered that duplex soils are better for the production of pasture systems than sandy soils (Moore 2004; Blume *et al.* 2016).

2.2.1 Soil types of the Swan Coastal Plain, Western Australia

The SCP is a narrow geographic area less than 40 km wide and is covered by sedimentary material. The eastern boundary follows Whicher Scarp from the south, then north along the Darling Scarp from Burekup to Muchea, and north-west along the Gingin scarp (Moore 2004). There are 11 soil types on the SCP and a series of dune systems located near the coast that formed as a result of sedimentary deposits from the ocean (Bolland 1998). The distribution of these 11 soil types is shown in Figure 2.3. The SCP is extensively cleared of native vegetation for agriculture or urban usage and supports most of the population of Western Australia.

The three dune systems of the SCP run parallel to the Indian Ocean, with alluvial plains located further from the coast as summarised by (Moore 2004). The coastal edge contains beach ridges and parabolic dunes, known as the Quindalup dunes. Behind this first system lie dunes of siliceous sands overlying limestone – the Spearwood dunes. The third system, the Bassendean dunes, is a complex of low dunes, sandplains, swamp flats and poorly drained plains. On the eastern side of the coastal plain are flat and often poorly drained alluvial plains (Pinjarra Plain), which meet the foot-slopes of the adjoining scarps (Ridge Hill Shelf) along the eastern edge (Bolland 1998). Once this landscape is reduced into dunes, it can be eroded by winds. This eroded sand is mostly from the dunes nearby the ocean and then redeposited on the dunes further inland, with the second major soil type formed by this redeposited erosion (Bolland 1998). A description of the dominant soil types of the SCP and the corresponding Australia Soil Classification (ASC) are outlined in (see Table 2.1).

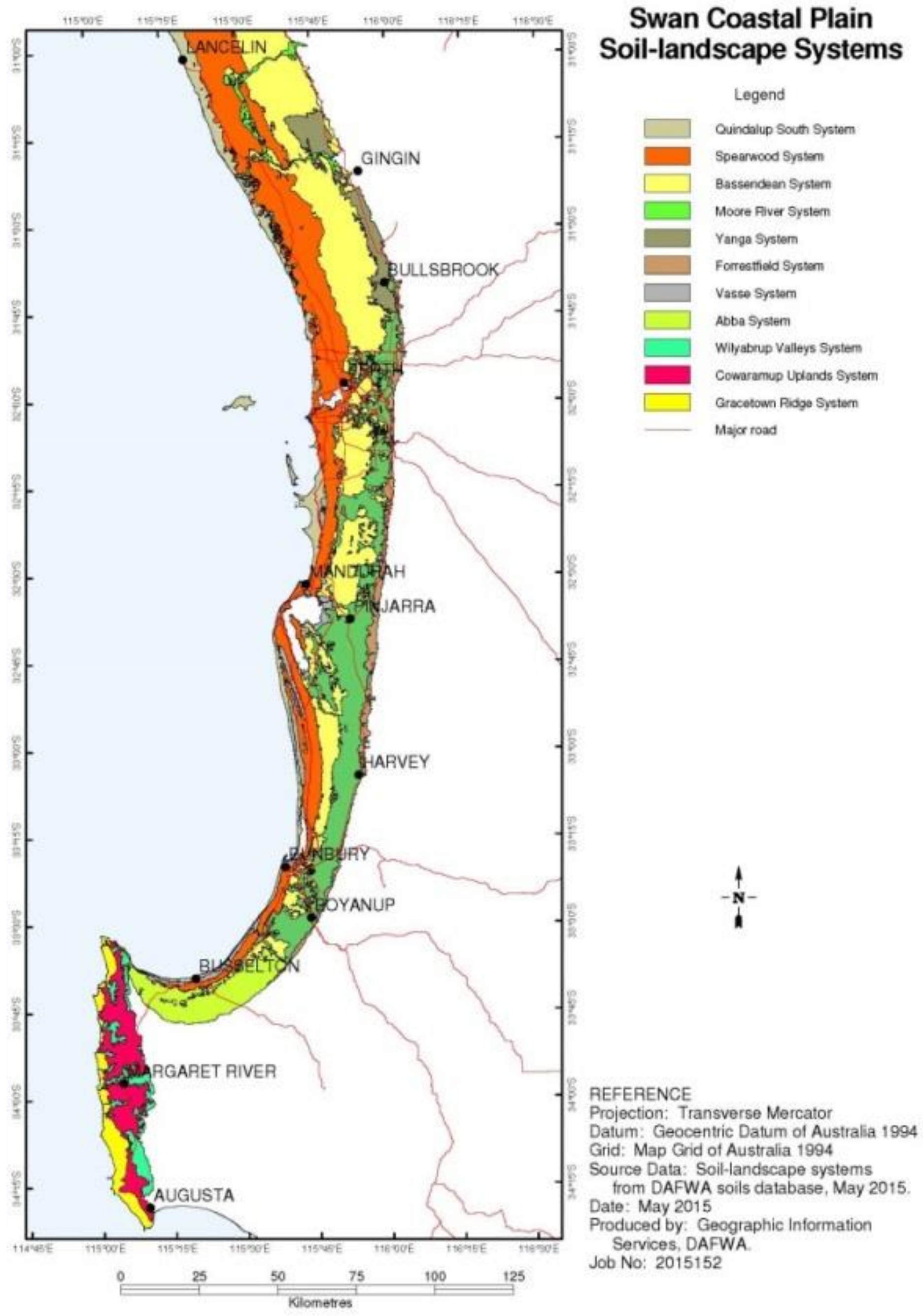


Figure 2.3 Soil-landscape systems map of the Swan Coastal Plain. Soil types are explained in detail in Appendix 9.2.1 (Gool *et al.* 2005).

Table 2.1 Dominant soil types of the Swan Coastal Plain (Moore 2004).

Location	Soil description	WRB*
Quindalup dunes	Calcareous deep sands.	Calcaric Fluvisol (McArthur 1991)
Spearwood dunes	Dominant soils are yellow deep sands, yellow to brown shallow sands.	Cambic or Ferralic Arenosol (McArthur 1991)
Bassendean dunes	Dominant soils are pale deep sands with brown deep sands on the poorly drained plains. Areas of the wet sand and bog iron soils are also found in swamps.	Orthic Podsol or Ferralic or Albic Arenosol (McArthur 1991; Bolland 1998)
Pinjarra Plain	Dominant soils are deep sandy duplex soils, shallow duplex soils, brown sandy earths, brown shallow loamy duplex soils and brown loamy earths. Minor areas of poorly drained cracking clays and red-brown non-cracking clays along the western margins. Brown sandy earths and brown loamy earths on recent alluvium.	Xanthic Ferralsol or Plinthic Ferralsol (McArthur 1991)
Ridge Hill Shelf	Dominant soils are sandy gravels, yellow deep sands and pale deep sands.	Xanthic Ferralsol or Chromic Luvisol (McArthur 1991)

* World reference base (WRB) (Salama *et al.* 2000; Schoknecht 2013; Isbell 2016).

Salama *et al.* (2000) studied the soils from the southern region of the Gnangara Mound on the SCP to determine the soil-water properties and nutrient leaching capacity of the soil. The physical, chemical and hydraulic characteristics of the topsoil (0–15 cm) and the subsoil (40–50 cm) were measured at 21 locations that represented the different land uses with the main soil types. Physical analysis of the two major dune systems the Bassendean and the Spearwood indicates that Bassendean sands contain the highest percentage of coarse sand particles and therefore have a higher hydraulic conductivity than the Spearwood dunes (Salama *et al.* 2000).

2.2.2 Soil organic and inorganic phosphorus

Components of the soil contain plant nutrients, of which P is stored in two forms – inorganic (Pi) and organic (Po) – and these P forms interact in the soil via complex processes (Yang *et al.* 2012a; Nash *et al.* 2014). Phosphorus is dynamic in the soil and undergoes a number of complex processes that have been described by (Sanyal and Datta 1991; Shen *et al.* 2011). The transformation of soil organic P is complex and can be organised into a conceptual model as shown in Figure 2.4 (Stewart and Tiessen 1987).

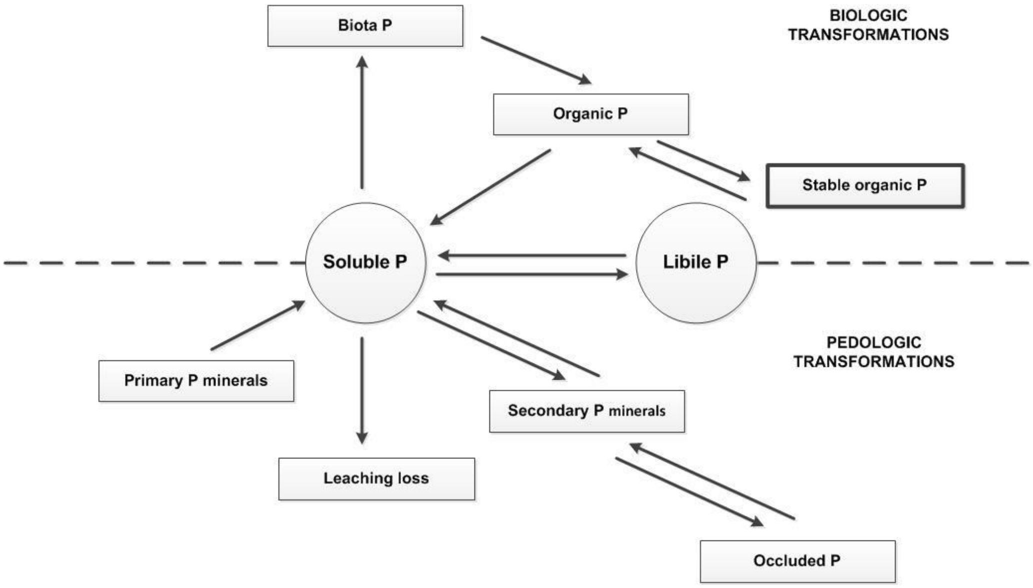


Figure 2.4 Phosphorus transformations in natural soil ecosystems (Smeck 1985). Soluble phosphorus (P) is also inorganic phosphorus.

Microbial uptake of P and its later release and distribution through the soil plays a critical part in the organic P cycle (Smeck 1985). Phosphorus fertilisers manufactured from rock phosphate are inorganic, and when applied to the soil, they can undergo a number of processes. These processes are dependent on the chemical and physical properties of the fertiliser (granule size) and the soil (PBI) that determine how P goes into soil solution and the proportion that can be taken up by the plant. The PBI is a measure of the sorption and indirectly how much P enters into solution. Soils have different binding capacity to sorb P which is generally increased with increasing clay content. This is because clay particles have an increased surface area for P sorption to take place (Stone and Mudroch 1989).

The rhizosphere is the interface between the soil and the plant and delineates the amount of P that the plant can access via, P diffusion, P transformation, P mobilisation, P adsorption, Pi transporter and microbial activity (Shen *et al.* 2011; Cesco *et al.* 2012; Dotaniya and Meena 2014). Phosphorus is absorbed by plant roots in the inorganic P form and that microbes and enzymes are critical for the mineralisation of soil organic P (Chen *et al.* 2002). Phosphorus in soil solution is readily accessible by plants, and this form of P (PO_4^{3-}) can be readily taken up by roots of which it is normally taken up as hydrogen phosphate ion (HPO_4^{2-}) (Black

1968). The amount of available inorganic P in solution is dependent on soil properties such as clay, aluminium and iron oxides, the amount of primary minerals such as apatites, and secondary P minerals such as calcium, aluminium and iron phosphate. Phosphorus can occur in organic forms and be released from microbial activities as stabilised P (inositol phosphates), and/or active P (orthophosphate dieters, monoesters, organic polyphosphates).

The cycle between inorganic and organic P can provide a significant amount of P that is available to the plant. However this requires large amounts of organic matter of at least 11%–13% (Shand *et al.* 1994; Williams *et al.* 1999). As soil organic matter is increased, the soil structure often improves to absorb more nutrients (Shepherd *et al.* 2002). Australian soils are generally low in organic matter Dalal and Chan (2001) with most soils from the SCP generally less than 4% organic carbon. The amount of plant available P from this cycle (i.e. low organic matter), is significantly less on these soil types compared to other Australia soils and hence requires the inorganic application of P fertiliser annually to maintain pasture production. In general, the application of P fertilisers has resulted in the increased retention of total P average 105% increase, Pi (154%) and Po (49%) when compared to their natural controls (Samadi and Gilkes 1998).

2.2.3 Measurement of phosphorus and concentration in soils

The measurement of P in soil can broadly be broken into two categories: 1) plant available P (PaP); and 2) total P (TP). The current methods for measurement of PaP include Olsen, Bray, Diffusive Gradient in Thin Films, and Colwell of which Olsen is currently the most commonly used method (Sparks *et al.* 1996; Christel *et al.* 2016). Currently, there is no globally adopted standard for P measurement.

The Olsen method was first developed in 1954 and estimates the availability of P in soils by extraction with sodium bicarbonate (Olsen *et al.* 1954). The Bray method can also be used to determine the amount of PaP and TP (Bray and Kurtz 1945). The Colwell P method is a measure of P in the soil that is available for plant uptake and is a modified version of the original Olsen method (Olsen *et al.* 1954; Awty 2011). The Olsen method is used widely in the United States of America (USA) and the eastern states of Australia. The advantage of the Colwell method is it can more accurately determine PaP at lower levels on the light soil types found in Western Australia (Bolland *et al.* 2003). Total P is a measurement of all P within a soil regardless if it is plant available or not (Allen and Jeffery 1990b). A more detailed description of these soil methods is outlined in Table 3.4.

Soil P can be defined into a number of categories, with these levels defined as a value or range through uses of the bicarbonate-extractable P and acid-extractable P methods as outlined in Table 2.2. Long-term applications of P fertilisers can increase total P levels by up to 300 percent from the original measured values in a soil (Colwell 1965).

Table 2.2 Ratings for bicarbonate-extractable P and acid extractable in air-dried soils from north-east Australia (Bruce and Rayment 1982).

Rating	Value/range (mg/kg) of phosphorus
Very low	< 10
Low	10–20
Medium	20–40
High	40–100
Very high	> 100

The natural amount of P within soils can vary widely between soil types, land use and each country's topography as outlined in Table 2.3. A comparison of unfertilised soil from the USA and Australia (as shown in Table 2.3) demonstrates that soil within Australia has a much lower natural P level.

Table 2.3 Comparison of Australian and United States surface soil measured for total phosphate content – modified from (Wild 1957).

Source of data	Number of samples	Phosphate content (% P_2O_5)
United States (Marbut 1935):		
Podzols (Rustic Podzol)	7	0.11
Grey-brown podzolic (Densic Podzol)	29	0.16
Red podzolic (Xanthic Podzol)	47	0.08
Prairie soils (Albic Lixisol)	11	0.13
Chernozems (Ferric Lixisol)	13	0.19
Dark brown soils (Dystric Arenosol)	9	0.15
Grey desert soils (Albic Acrisol)	6	0.24
Australia, all soils weighted according to survey area (Wild 1957):		
HC1-soluble phosphate	2217	0.047
Total phosphate (calculated)		0.069

The soils within the SCP also have differing inherent levels of P which has generally increased due to agriculture and horticulture production (McArthur 1991). With the range of soil types on the SCP and the land use history, the soils will range in TP levels which will determine the required amount of P fertiliser for maximum pasture dry matter yield (see Table 2.4) (Bolland 1998). The analysis of this soil indicates that there is a differing potential to P leaching on the SCP that cannot be corrected with a single fertiliser strategy.

Table 2.4 Total phosphorus measured in soils collected from uncleared, previously unfertilised native vegetation on the Swan Coastal Plain, Western Australia.

Soil	Total P[A] (mg/kg P per grams of soil)
Coastal dunes	
1. Quindalup dunes	290
2. Spearwood dunes	
(a) Cottesloe	190
(b) Karrakatta yellow phase	44
(c) Karrakatta grey phase	22
3. Bassendean Dunes	
(a) Jandakot	18
(b) Joel	30
Pinjarra Plain Soils	
(a) Coolup	52
(b) Wellesley	180
(c) Boyanup	120
(d) Blythwood	130
(e) Dardanup	510

[A] Determined by digesting the soil in concentrated sulphuric acid and measuring the concentration of phosphorus in the digest (Bolland 1998).

2.2.4 Measurement of soil ability to retain phosphorus

The ability of soils to retain P is measured as an index. The two common indexes used in Australia are the Phosphorus Retention Index (PRI) and the Phosphorus Buffering Index (PBI). The PRI is a measure of the soil's relative ability to extract P from solution mixing a quantity of soil in solution with a single amount of P for a set period of time. The amount of P remaining in solution measures the soil's ability to fix P (Allen and Jeffery 1990b; Bolland *et al.* 2003). In Western Australia there are a number of measurements used to determine the order of the soils ability to absorb P. The measurement of the amount of extractive iron from the soil by using ammonium oxalate (AmOx-Fe) or reactive iron was a method of determining how much P will be retained by a soil (Bolland *et al.* 2003). The PRI measurement is preferred over the reactive iron method due to the soil's PRI decreasing with the saturation of absorption sites with the addition of cumulative inputs of P fertiliser over time; however, the P levels remain constant when tested using reactive iron.

Phosphorus Buffering Index (PBI) is similar to PRI except that a range of P rates are mixed with the soil, and the index is adjusted for pH (Quinlan and Wherrett 2016). As a soil's PBI level increases, its capacity to absorb applied P increases and these indexes will be the nominated soil comparison method to retain applied P fertiliser used in this research (Moore 2004). Phosphorus buffering index can be used in conjunction with Colwell P measurement to give an indication of the soil's ability to 'lock' up P. Phosphorus buffering index is measured on a scale of 1 to 800 and PRI is measured on a scale of 1 to 100 (see Table 2.5). The combination of the PBI and Colwell P measurement is generally used to provide producers with a recommended fertiliser rate (see Figure 2.5). Soils with a greater PBI have a greater ability to adsorb P onto soil exchange sites, and therefore it becomes unavailable to plants (Moody and Bolland 1999). Soils with lower PBI retain less P and therefore leave most of the P applied from fertiliser available to plants. Low PBI soils are also at an increased risk of losing P to leaching, owing to its reduced ability to hold onto applied P. Managing soils with higher PBI usually involves increasing the application rate of P fertiliser over a number of years. This would help to build up soil P levels so that it reaches a level that is available to the plant (Price 2006).

Table 2.5 Phosphorus soil indexes rating and values. Phosphorus buffering index (PBI) and phosphorus retention index (PRI). The method of converting PBI to PRI values is outlined by (Bolland and Windsor 2007).

P buffering capacity category	PBI values	PRI values
Extremely low	< 15	1
Very very low	15–35	2
Very low	36–70	15
Low	71–140	38
Moderate	141–280	100+
High	281–840	100+
Very high	> 840	100+

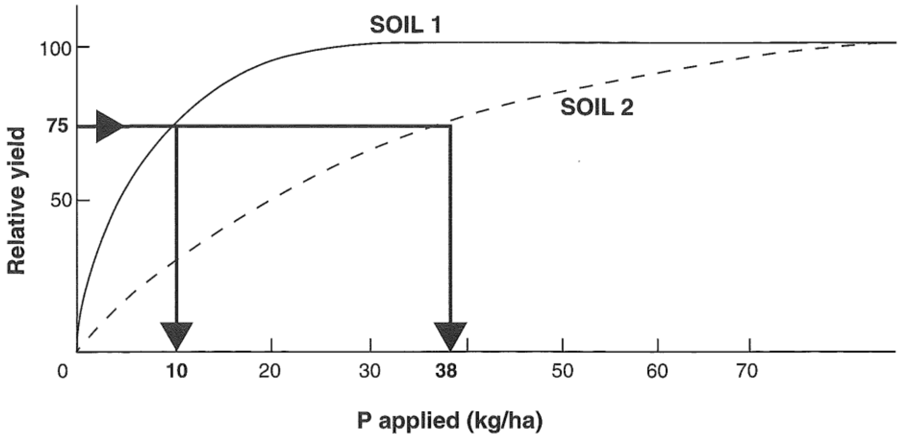


Figure 2.5 The relationship between the percentage maximum (relative) yield and the amount of P fertiliser applied for 2 different soil types. The P was applied as single superphosphate in the current year of a soil with a low capacity to retain P (soil 1) and on a soil with a high capacity to retain P (soil 2) (Bolland and Gilkes 2001).

2.2.5 Forms of phosphorus in the soil

Within the soil, P can exist in different forms but P contained within the soil can only exist in one of three pools (solution P, active P or fixed P) (Busman *et al.* 2009; Damon *et al.* 2014b). The solution pool is relatively small and usually contains only a few kilograms of P per hectare. The P within this pool is usually in the orthophosphate form. However it may contain small amounts of organic P. Orthophosphate is the only form of P that plant can assimilate as outlined by (Heckrath *et al.* 1995). This pool is important because it is the one that plants can access and has considerable P mobility. The majority of the P assimilated by the plant during the growing season may have only moved a few centimetres from the soil to the plant roots. Rapidly growing crops can quickly exhaust the P in this pool if it is not continuously replaced (Bünemann *et al.* 2011).

The active pool contains P that is in a solid phase and which is easily released into the soil solution surrounding the soil particle. As the plant assimilates P, the P amount in the solution decreases and some of the P from the active pool is released. This is due to the small size of the solution pool that is the primary source of P in close proximity to the root for plant use. The ability of the active pool to replace P into the solution P within the soil is considered as fertile soil in regards to P. Within a paddock, the soil P may vary between several kg/ha to containing several hundred kg/ha in the active pool depending upon soil type. This pool will contain inorganic P that is bound or adsorbed to the small soil particles. The P that has reacted with other elements such as calcium or aluminium can form soluble solids and/or organic P that is somewhat soluble and is more easily mineralised. The adsorbed phosphate ions are retained onto the active areas on the surface of a soil particle. The amount of adsorbed P within the soil increases as the amount of P in the soil solution increases and vice versa. The soil particles can either act as a P source or store with the water surrounding the soil particle depending on the soils condition (Holtan *et al.* 1988).

The fixed pool contains the inorganic P compounds that are highly insoluble and organic compounds that are highly resistant to mineralisation by microorganisms. Phosphorus within this pool can remain within the soil for a number of seasons without becoming available to plants and in general, does not increase soil fertility. Inorganic P compounds within this pool have a more crystalline structure and are less soluble than the compounds in the active pool. There is some slow conversion between the fixed and active pools within the soil (Hocking *et al.* 1997).

2.2.6 Absorption and leaching of phosphorus in soils

After water-soluble P fertiliser is applied to soil, a series of reactions occur between P, soil constituents and non-P components of the P fertiliser that can remove P from the solution phase and thus make it less plant available (Hedley and McLaughlin 2005). These reactions may include adsorption to the surface of the soil particles, diffusion where P becomes bound to the soil particle and precipitation that forms new solids in the soil. In acidic and neutral soils, there are fast and reversible surface-based absorption reactions where P moves into the soil of Al and Fe oxides (Strauss *et al.* 1997). Phosphorus applied to soil will be adsorbed onto soil particles until the soil particles become saturated and unable to absorb anymore P, with any residual P in the solution being vulnerable to being lost to leaching (Pierzynski *et al.* 2005; Andersson 2016). An important factor altering the extent of the absorption rate, particularly in neutral or acidic soils, is determining the abundance and type of aluminium and iron present in the soil (Borggaard *et al.* 1990). Adsorption reactions are therefore key processes regulating the efficiency of added P fertiliser, however when P concentration is increased (i.e. around fertiliser granules) with precipitation reactions of P, the type of fertiliser becomes an important consideration (McLaughlin *et al.* 2011).These precipitation reactions involve the creation of new solid phases from ions in solution and can be seen around fertiliser granules as shown in Figure 2.6 (Hedley and McLaughlin 2005).

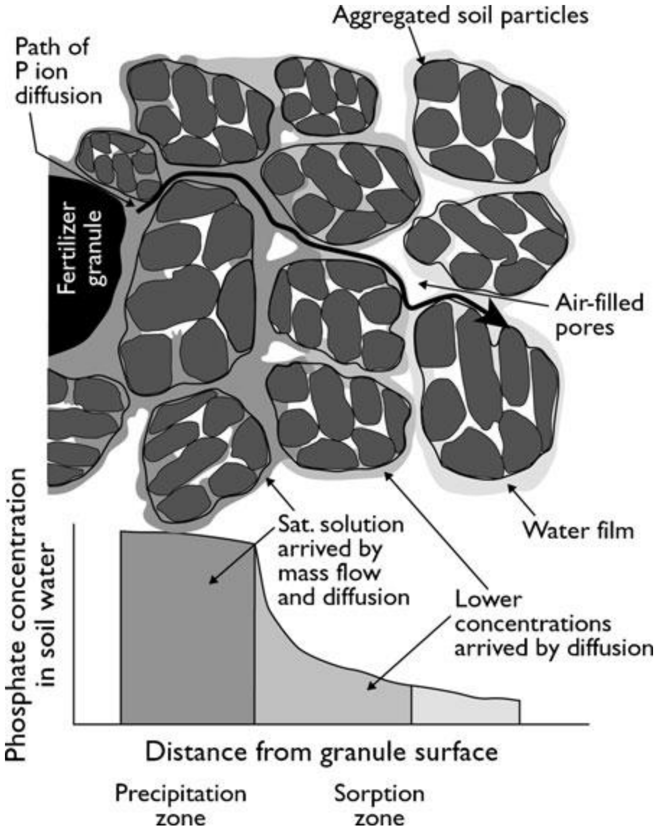


Figure 2.6 Diagrammatic representation of the movement of phosphate. The movement of phosphate by mass flow and diffusion from a granule of water-soluble P fertiliser through water-filled and water-lined large micropores in a well-aggregated soil. Note that the penetration of P into aggregates is incomplete due to the slow rate of P diffusion in smaller, intra-aggregate microspores and discontinuous microspores (not to scale). This is copied from (Hedley and McLaughlin 2005).

Phosphorus is quickly released from water-soluble P fertiliser granules with most of the P leaving the granule within days of application to the soil (Williams 1971b, 1971a; Benbi and Gilkes 1987). There is a strong relationship between the soil’s absorption capacity and the potential for applied water-soluble P to be leached through the soil profile (Shober and Sims 2007). If a soil has a low adsorption capacity and large aggregated soil particle sizes (small surface area), such as sand, the ability to retain P is reduced. The combination of low soil adsorption capacity and high rainfall results in an increased risk of dissolved P rapidly diffusing below the rhizosphere. Phosphorus sorption is the capacity of the soil to adsorb P and this capacity greatly influences the yield response and soil analysis calibration curves. As the capacity for the soils to absorb P increases, the P fertiliser application must also increase to maintain the same yield (Moore 2004).

2.2.7 Nutrient availability in soils

Within the soil, there is a nutrient interaction with the soil that determines the nutrient availability to the plant. These interactions change over time and can include: the adsorption and/or release of nutrients, conversion through plant activity, moisture, temperature, microbial activity, management practices and pH (Brady and Weil 1996; Barré *et al.* 2007; Delgado-Baquerizo *et al.* 2016; Niu *et al.* 2016). Phosphorus availability in the soil is a complex process that is dependent on a large number of factors that influences how the plant can access any applied P of which pH is a critical interacting factor (Rajan *et al.* 1991; Azhar *et al.* 2013). From these interacting factors, pH is one that can be reasonably controlled with the application of lime (Dick *et al.* 2000).

The solubility of different inorganic phosphates directly affects the plant's ability to assimilate P. A pH between 6 to 7 is optimal for plant uptake (Oldham 2014). When the soil pH is lower than 6, P can become bound up in the aluminium phosphate form. As the acidity of a soil increases to below 5, P can also be fixed as iron phosphate. As soil alkalinity increase above 7.3, P becomes fixed as calcium phosphates. Inorganic P has a negative charge in most soils which is due to phosphate ion (PO_4) reactivity with positively charged iron (Fe), aluminium (Al) and calcium (Ca) ions to form relatively insoluble substances. If this happens, the P is considered adsorbed and will not go into the solution pool for the plant to access (Cho and Caldwell 1959).

Soil acidity has a large influence on P with the amount of soluble organic P that is available to the plant particularly on soils that have low fertility (or P binding) levels (Bolan *et al.* 1986; Vaz *et al.* 1993). The availability of different P binding elements varies at different pH with the optimum level to access all elements is between 6.5 and 7.2 (Truog 1939; Sonneveld and Voogt 2009). These levels are outlined in Figure 2.7 and, for P; the optimum available level is between 6.5 and 8.0, with P also becoming more plant available once the soil becomes more alkaline from 8.6 to 10.0. Rhizosphere acidification and soil pH does not necessarily increase phosphate solubility (Staunton and Leprince 1996). Carboxylates, the conjugate bases of organic acids could have an important role improving soil phosphate availability (Lambers *et al.* 2002).

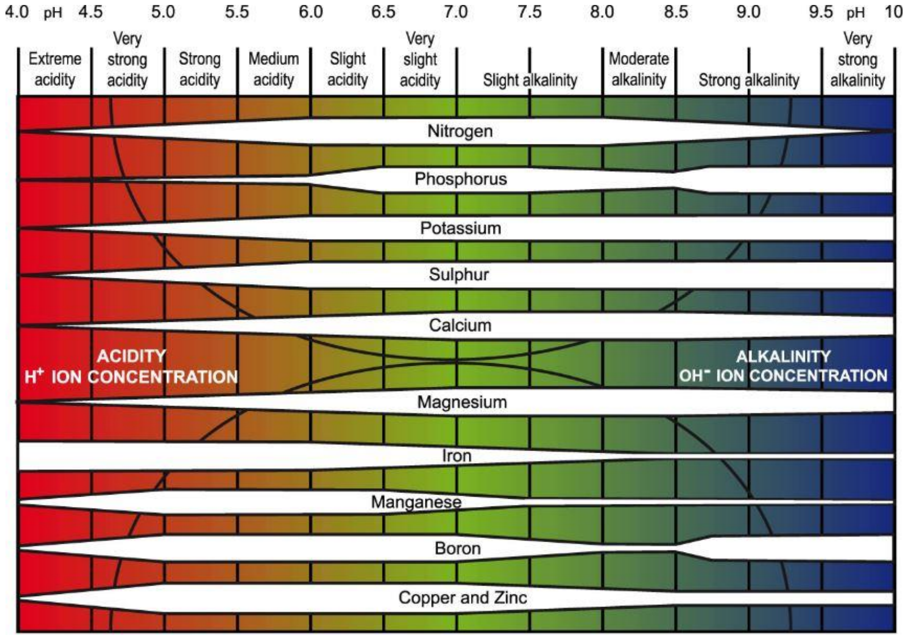


Figure 2.7 Diagram illustrating general trend of relation of soil reaction (pH) and associated factors to the availability of plant nutrient elements (Truog 1939).

Each element is represented by a band as labelled. The width of the band at any particular pH value indicates the relative favourableness of this pH value and associated factors to the availability of respective elements in question in readily available forms (the wider the band the more favourable the influence), but not to the actual amount necessarily present, this being influenced by other factors, such as cropping and fertilisation. The width of the heavily cross-hatched area between the curved lines at any pH is proportional to the hydrogen-ion concentration (intensity of acidity) less than pH 7, and to the OH-ion concentration (intensity of alkalinity) greater than pH 7 (Truog 1939). The application of lime to increase the pH of acid soils can influence the availability of P as described by Haynes (1982) and liming can increase the availability of P through stimulating mineralisation of soil organic P. However, soils that have a high pH; insoluble calcium phosphate can precipitate and reduce the amount of available P (Nahas 1996).

2.3 Environment

The environment in the context of pasture production systems is the area that is being used for the production of crops and the surrounding area that can be influenced by this production. The environment includes rainfall, soil temperature, soil type, landscape and waterways that are utilised during the plant growth cycle in these production systems. Traditionally, nutrient applications were orientated towards optimising economic returns from applied nutrients for crop production (Beegle *et al.* 2000). Currently, the agronomic and economic return of nutrient management remain important, however, in addition to this, the process must now consider the possible impact of applied nutrients to the environment (Haygarth *et al.* 2009). The nutrient application and management process is critical for maximising the economic benefit from applied nutrients while minimising the possible environmental damage (Radcliffe *et al.* 2009). The decision to apply nutrients to an agricultural environment should follow a process that should include, assessment, analysis, decision making, evaluation and refinement (Withers *et al.* 2009). There have been some factors identified as critical to implementation and success of nutrient-management which include: engagement by all key stakeholders, full utilisation of established infrastructure, focused nutrient management planning, voluntary vs. mandatory implementation, and the economic benefit of nutrient management (Maguire *et al.* 2009).

Phosphorus loss from fertiliser is a significant problem that has caused environmental damage to aquatic environments (Sharpley *et al.* 1994a; Zimmer *et al.* 2016). The protection of these aquatic environments requires the reduction of nutrient inputs from P fertilisers into these ecosystems (Chen *et al.* 2016). The growth of algae removes oxygen from the water, resulting in an increase in fish deaths from asphyxiation and a general decline in river system health (Hodgkin and Hamilton 1993).

2.3.1 Seasonal climatic impact on agriculture

Seasonal changes to the environment are generally from a change in rainfall and temperature over the time for plants to complete their growth cycle. These changes can have a significant influence on the growth of crops and pastures and the transformation of nutrients within agricultural systems (Marshall *et al.* 2016). Generally, moisture is the most limiting factor in dryland agricultural systems in the growing season, and subsequent yield potential is determined by the rainfall pattern of a region (Zhang *et al.* 2016). Rainfall is critical to increasing soil moisture and the availability of P but excess amounts of moisture will result in the leaching of P from agricultural systems (Hahn *et al.* 2012). To quantify P loss from the influence of rainfall and P forms with differing water-soluble content, as discussed in a research study conducted by Shigaki *et al.* (2007), that showed the movement of P was increased with the amount and intensity of rainfall. The P movement was for both dissolved P in solution and P particles. The study concluded that the water soluble content of P fertiliser and rainfall intensity had a major influence on P movement in the runoff, which is important in evaluating the long-term risks of P source application on P movement from agricultural systems.

Temperature changes can impact on the availability of P and other nutrients within the soil (Zingaretti *et al.* 2013). These changes in soil P availability may reflect in the uptake by plants or mineralisation–immobilisation within the soil (Chen *et al.* 2003). Variations over a season in some soil P fractions have been observed by (Shi *et al.* 2015). The changes were observed in winter for all soil P fractions and showed significant soil P transformation and movement over this period. This study showed that P in soils changed during winter months as a result of changes in the amount of labile P fractions, this could have been due to the solubilisation of applied P fertiliser combined with possible environmental factors. In pasture soil labile organic P, microbial biomass P and organic debris can increase over winter and decrease in spring. This has been attributed to increasing mineralisation and plant uptake during spring and the lower temperature activity of microbes and P mineralisation during winter (Perrott *et al.* 1992; Frossard *et al.* 2000).

In the future as the climate changes, there could be a significant increase in P movement and eutrophication of waterways in selected regions of the USA (Jeppesen *et al.* 2009). Phosphorus export from agricultural systems into waterways is expected to increase in the USA due to higher winter rainfall and increasing temperatures. Modelling has suggested that P exports could increase by 3.3% to 16.5% in the next 100 years depending on soil type and region. In lakes, higher eutrophication could be expected, reinforced by the temperature-mediated increased release of P already present in sediment (Jeppesen *et al.* 2009).

2.3.2 Global loss of phosphorus to the environment

The removal and redepositing of P can significantly reduce soil fertility in a region (Heathwaite *et al.* 2003). Erosion can result in P loss for applied fertiliser at rates equivalent to that of removal by plants (Quinton *et al.* 2010). This problem is global and is not limited to a single location with rates of N and P loss to erosion outlined in Figure 2.8.

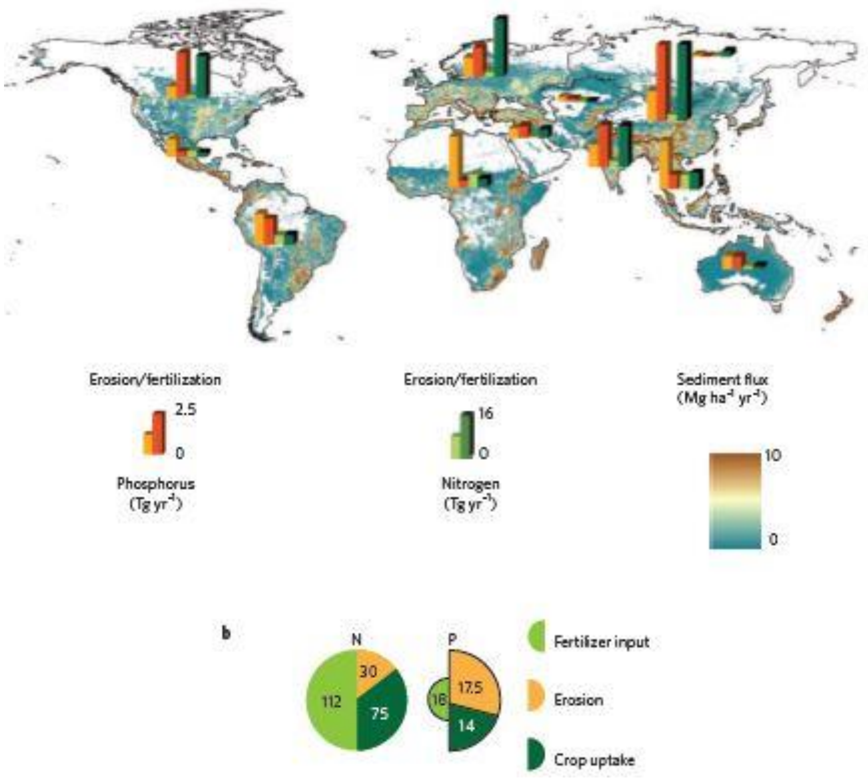


Figure 2.8 Global fluxes of sediment, nitrogen and phosphorus. Shaded areas show the global distribution of sediment fluxes and information bars show the continental fluxes of nitrogen and phosphorus by water and tillage erosion compared with fertiliser use. Global fluxes of nitrogen and phosphorus (Tg yr^{-1}) due to fertiliser input, erosion and crop uptake (Quinton *et al.* 2010).

Soil testing has often been used to estimate the risk of P exports associated with agricultural production systems although variability exists and further investigation is required (Nash *et al.* 2007). The relationship of soil P analysis is defined by (Olsen *et al.* 1954; Colwell 1965; Sims *et al.* 2000) and can be used to determine the potential for P export. Nash *et al.* (2007) concluded that the Colwell P soil test provides a better correlation to P export risk than the Olsen soil test. It was also concluded that a large study was required to define the relationship between soil P tests in Australian soils for the purpose of assessing P loss (Nash *et al.* 2007).

2.3.3 National loss of phosphorus to the environment

The landscapes of the Australian continent are generally flat, but even with this topography area of soil erosion still can occur that will reduce agricultural productivity (Prosser *et al.* 2001). It has been estimated that approximately one-half of Australia’s agricultural and pastoral lands are at risk of erosion and will require protection (Loughran 1989). There are a number of ways that P applied to the soil can be lost to the environment from the pasture production system and these factors can be broadly broken down into two categories, geographical and environmental (Quinton *et al.* 2010). The geographical factors are soil type, soil moisture content, location, and slope of the paddock (Singh and Thompson 2016). The environmental factors are management practices, rainfall timing and volume, crop, and wind speeds of the location. All these factors contribute to the loss of soil P and will determine how much and at what rate P is lost from the pasture production system (Sharpley *et al.* 1994b). The physical movement of soil is generated by water and the wind. Water can both cause leaching and surface topsoil erosion while wind can remove any loose light topsoil. A number of physical methods can be implemented to reduce P physical movement with these methods (see Section 2.2.5) based around the reduction of water and wind speeds across the soil surface (Sakadevan and Bavor 1998; Sharpley *et al.* 2003; Hart *et al.* 2004). Methods used to reduce soil and nutrient erosion from water erosion are, contour banks, drains that reduce the surface speed of water and its ability to pick up topsoil where P is contained. For wind erosion, the most commonly used methods are, cover crops, stubble retention from winter crops’ and windbreaks such as trees to reduce wind speed, and the ability of the wind to remove dry soil over the summer months. Soil physical structure and profile has a major influence on the movement of P down the soil profile and will affect the rate of leaching and where P settles in the soil.

2.3.4 Phosphorus loss on the Swan Coastal Plain

The geographical location of the SCP is flat with a gentle gradient down to the major waterways and Indian Ocean. The majority of farming systems on the SCP are rain fed and generally have no cover crop over the summer months. This type of agricultural system means that the loss of P from the pasture production as physical erosion such as water and wind action of the topsoil is relatively low. The major loss of P to the environment is caused by leaching by winter rainfall which ends up in the waterways and estuaries of the Swan-Canning, Peel-Harvey, Leschenault, Vasse-Wonnerup and Hardy Inlet in Western Australia. These areas are within the SCP due to the flat sandy soil topography of the SCP, increased eutrophication and discharge of P into the Peel-Harvey estuary are often through increased winter rainfall on lighter soil types (Summers and McLaughlin 1996). Reducing environmental damage to the SCP was prioritised in 2007 when the Western Australian Government released the ‘Fertiliser Action Plan’, which outlined phasing out of high water soluble phosphate fertilisers. The phase-out process was to take place over four years, concluding with a total ban starting in 2010–11 (Cox *et al.* 2007).

There are substantial research findings from the catchments containing the river systems of the SCP indicating that at least a 50% reduction in annual P load is needed to significantly reduce the environmental damage to these river systems. Agriculture is the major contributor to the P pollution in these systems and it is estimated that annual P loss from pasture for beef and dairy production accounts for 64% of the total P (Cox *et al*. 2007). In addition to the Fertiliser Action Plan, the Western Australia Government released the ‘Swan-Canning river quality improvement plan’ in 2009, with the Swan River Trust determining that an annual reduction of 12 tonnes or 46% of P from these river systems was required to improve water quality (Cahill 2009).

2.3.5 Phosphorus export hazard on the Swan Coastal Plain

The P export hazard is defined as the susceptibility of P entering the river and surface waterways causing eutrophication (Gool *et al.* 2008). The export hazard from applied P fertiliser through the landscape is affected by some factors, including, landform, soil types, catchment size, drainage density, the location of drains, rainfall/runoff, climate, and the amount and type of vegetation within the landscape (Summers *et al.* 1999b). The main factors in eutrophication of most waterways are the total flow of water, time taken from application to entering the surface waterway, and the catchment size. These factors combine to create a P index that is used to determine the export loss risk of P from agricultural land (Lemunyon and Gilbert 1993; Benskin *et al.* 2014). When heavy rainfall occurs, rapid movement of water on a soil with a low PBI can result in P that cannot be absorbed will be lost to leaching (Summers *et al.* 1999b). Soil characteristics such as PBI and soil profile can influence P leaching due to the rapidly vertical movement of water, thereby reducing the contact time between soil particles and P in solution that may be insufficient for adsorption to occur (Koopmans *et al.* 2001). Figure 2.9 highlights the areas on the SCP that are most susceptible to P loss. The rating is determined by the most limiting factor and does not take into account P leaching into deep groundwater (Gool *et al.* 2005).

Frequent application of SSP to maintain agricultural production over a long period of time at some locations in the Peel-Harvey Catchment has led to a build-up of P in soils above the requirements for plant production (Richie *et al.* 1985). This excessive build-up of P has caused environmental damage due to the movement of P from soils with low PBI’s into waterways and sensitive areas (Richie *et al.* 1985). Richie *et al.* (1985) conducted a study within the Peel-Harvey Catchment to reduce P levels in soils while maintaining plant-available P in soils. The soil P levels were just adequate to maintain plant growth without causing further build-up in the soil P reserves. Their study found there is limited information and knowledge about the effect of repeated and long-term applications of adequate water-soluble P fertilisers. This limited information about the long-term application of adequate water-soluble P fertiliser outlines the need for long-term field experiments and laboratory research to improve knowledge about the long-term effect of reducing P levels in soil types on the SCP.

Phosphorus application rates below 2 kg/ha annually are recommended to prevent algae blooms (Richie *et al.* 1985). Algal blooms have not occurred in the Harvey River when the P loading is less than 2 kg/ha and P levels need to be maintained below this level. Phosphorus run-down times on deep grey sands (Joel Soil) and duplex sands (Coolup Soil) were studied to determine the time taken to reach a 50% reduction in P losses. The study concludes that it is not possible to reduce these soils P levels back to historic status (i.e. theoretical level) to stop P leaching without reducing pasture dry matter yields (see Figure 2.10 and Figure 2.11).

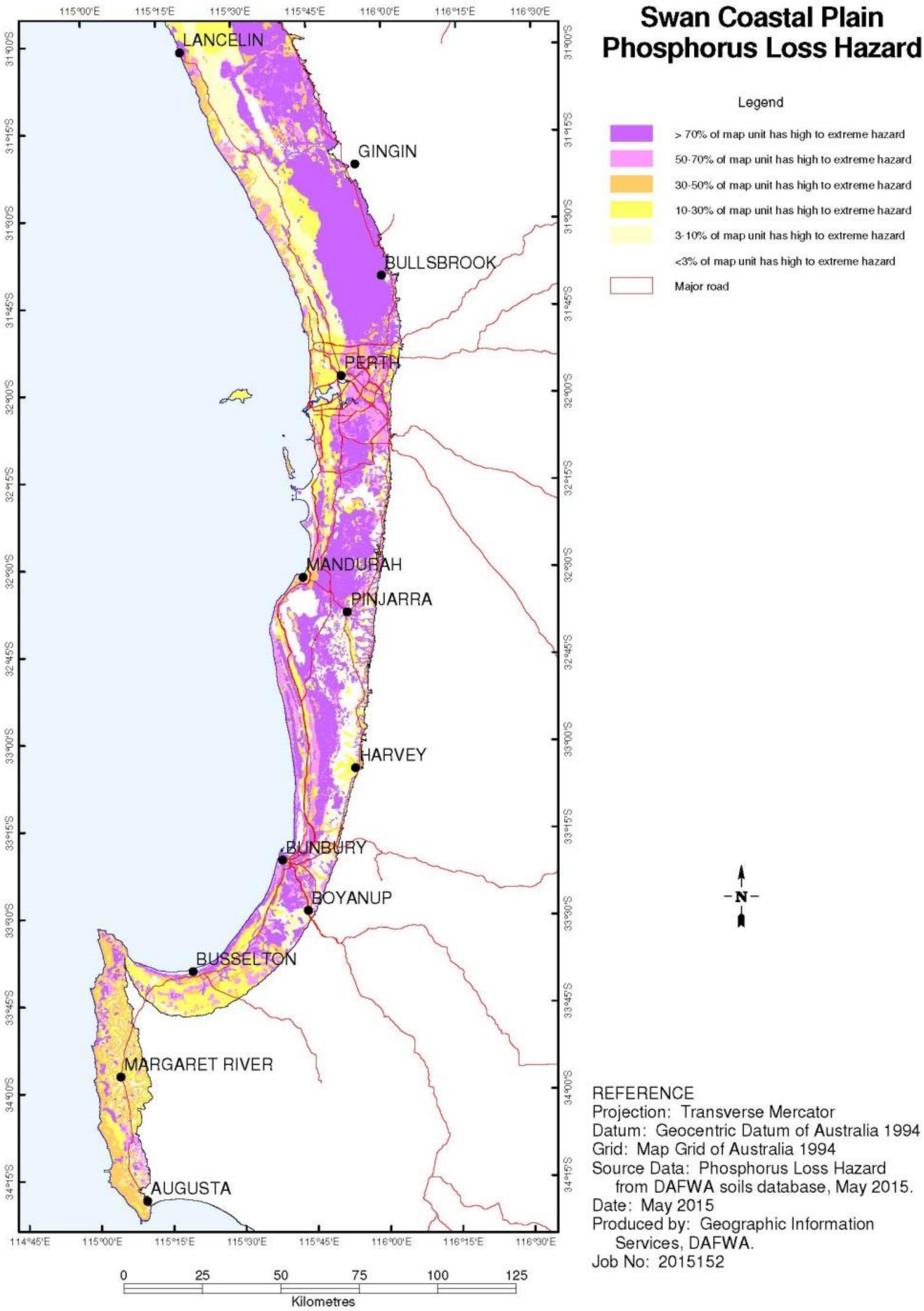


Figure 2.9 Phosphorus loss hazard map of the Swan Coastal Plain (Goulding 2015). The methodology to determine phosphorus loss hazard is outlined in Section 2.5.

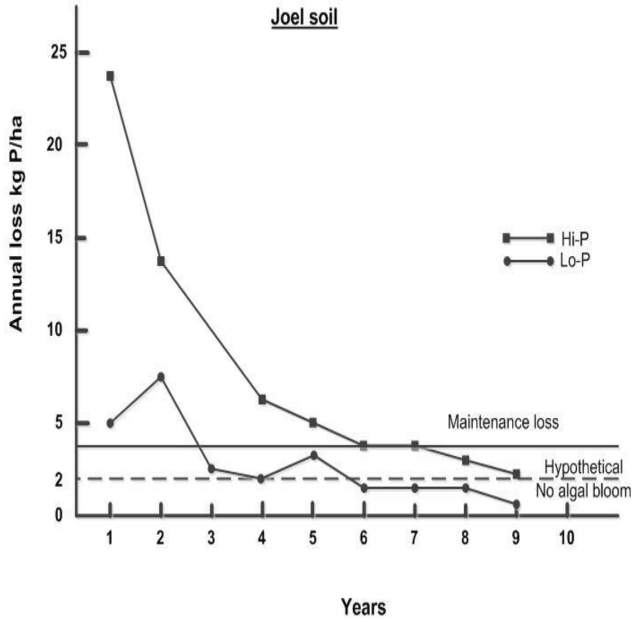


Figure 2.10 Variation in annual loss of phosphorus (kg/ha) with time (years) since fertilisation of deep grey sands ceased (Richie *et al.* 1985). Joel soil is classified as a Tenosol under the Australia soil classification guide (Schoknecht and Pathan 2013).

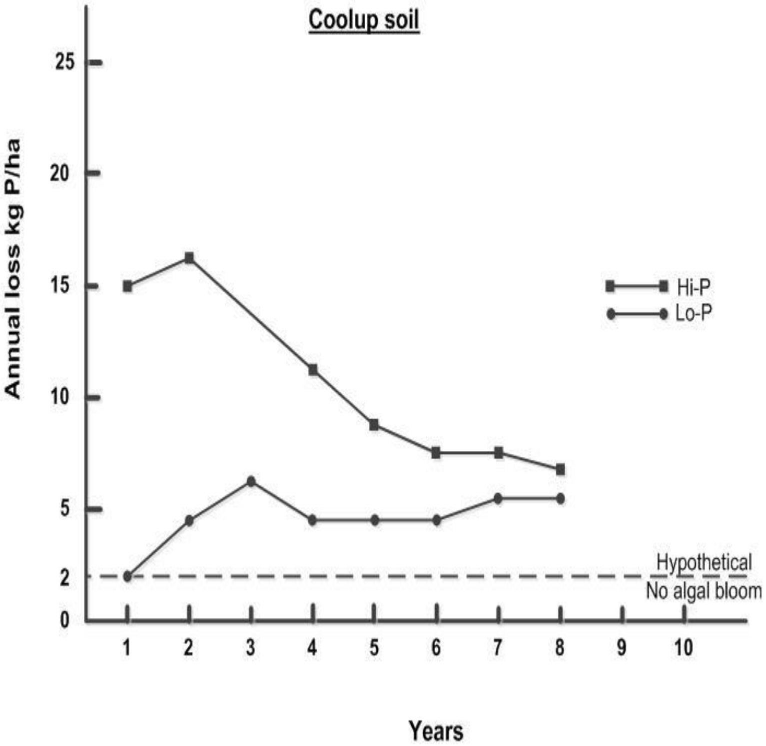


Figure 2.11 Variation in annual loss of phosphorus (kg/ha) with time (years) since fertilisation of duplex soils ceased (Richie *et al.* 1985). Coolup soil is classified as a Tenosol under the Australian soil classification guide (Schoknecht and Pathan 2013).

Richie *et al.* (1985) recommends that P levels in the soil be run down to that required for plant growth over a number of years and to replace SSP with a new coastal superphosphate (NCS). Applying superphosphate every second year or as required to maintain soil P levels at just above adequate levels for plant growth, will minimise P movement. However, it was outlined that changing superphosphate to NCS may not reduce P movement into the waterways due to a slower reversion and be moved in the following season (see Figure 2.12).

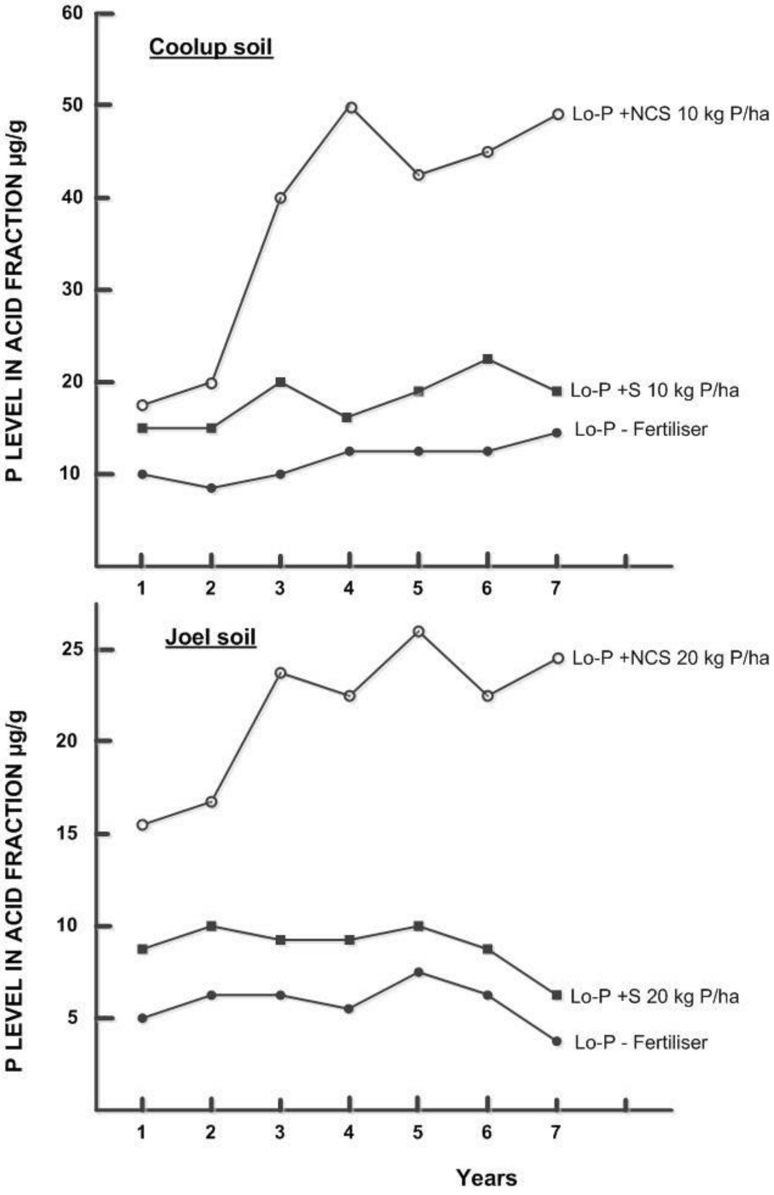


Figure 2.12 Phosphorus levels in the acid-soluble soil fraction and their variation with time and application of different fertilisers (Richie *et al.* 1985). Superphosphate (S) and new coastal super (NCS). Coolup and Joel soils are as Tenosol as classified under the Australian soil classification guide (Schoknecht and Pathan 2013).

2.3.6 Environmental effect of phosphorus loss on the Swan Coastal Plain

The Fertiliser Action Plan determined that highly water-soluble fertilisers were those containing more than 80% water-soluble P and that fertiliser with less than 40% water-soluble P for commercial broadacre farmers would reduce the total amount of P entering the waterways by the required amount (Cox *et al.* 2007). As outlined in Table 2.6, the analysis of current fertilisers used on the SCP, showed that all fertilisers have water-soluble well above the limit set by the Fertiliser Action Plan.

Table 2.6 Typical analysis of a range of high water-soluble P fertilisers.

Product	Total phosphorus (%)	Water-soluble phosphorus (%)
Single Super (‘Superphosphate’)	8.8	77
Double Super	17.1	80
Triple Super	20.7	78
MAP	21.9	83
DAP	20.0	89
‘Turf Special’	1.8	83
‘Potato E’	7	83

The Fertiliser Action Plan specified that the fertiliser industry had four years to find a replacement for high water-soluble P fertiliser and develop a cost effective lower water-soluble P (Cox *et al.* 2007). A number of replacements for low water-soluble P fertiliser were investigated and are outlined in Table 2.7 along with with their phosphate chemistry.

Table 2.7 Analyses of the new low water-soluble phosphorus fertilisers. This fertiliser was a mixture of separate granules of ordinary superphosphate and rock phosphate (Summers and Weaver 2008). Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP). The percentage of each form of phosphate (within the brackets) and NA indicates that the data is not available.

	Fertiliser	**Total P %**	**MCP**	**DCP**	**TCP**
Control	Superphosphate	9.2	7.56 (82.2)	1.46 (15.9)	0.18 (1.96)
A	Super + 23% bauxite residue	7.4	3.01 (40.7)	4.16 (56.2)	0.23 (3.11)
B	Optiphos1	8.6	3.63 (42.2)	4.66 (54.2)	0.31 (3.60)
C	Optiphos2	9.2	4.08 (44.4)	2.35 (25.5)	2.77 (30.11)
D	Summit LWSSP	15.4	NA	NA	NA

While the Fertiliser Action Plan was not implemented due to a change of government, research to reduce the problem of P loss from leaching continues as a research area. Eutrophication in surface waters (e.g. dams, lakes, estuaries and rivers), combined with physical-chemical factors (i.e. increased water inflow from rainfall) will continually lead to algal blooms (Robson and Hamilton 2003). The increase in algal growth deoxygenating the water and increase nutrient toxicity reducing the aesthetic value will result in changes the species diversity. These changes can also have a detrimental effect on drinking water and recreational use (Dougherty *et al.* 2004; McDowell *et al.* 2004; Drewry *et al.* 2006).

Phosphorus is often the limiting nutrient for algal growth in the shallow river systems on the SCP, and when P from fertiliser is leached and enters these river systems, resulting in large areas of algal growth recurring in the river systems (Engineers 1988; Hodgkin and Hamilton 1993). Wrigley *et al.* (1988) studied the P levels in waters of the coastal wetlands in agricultural areas of Western Australia. They analysed a total of 68 wetlands in this catchment area and found total P concentrations between 0.4 and 7.8 mg/L, with the higher P levels attributed to agricultural activities. The problem of eutrophication from agricultural fertilising has been detected at other locations in Australia, such as in the north-eastern wet-tropic cropping land in Queensland (Babare *et al.* 1997b). This problem is also not limited to Australia, with algal growth detected after a flood carried a large increase of P into a lake system in Wisconsin in the United States (Richardson and Vaithiyanathan 1995; Carpenter 2008).

2.3.7 Economical effect of phosphorus loss on the Swan Coastal Plain

Applying the correct amount of P fertiliser is critical to obtain the most economical pasture growth response (Cornforth *et al.* 1993; Morel *et al.* 2000). Phosphorus fertiliser is applied to pasture by broadcasting fertiliser across the surface of the soil before the break of the season (Price 2006). This method is used so that subsequent rainfall will dissolve P into the soil solution where it becomes available to plants. Phosphorus loss to the environment from the rhizosphere of a plant typically happens by surface runoff, and leaching. Phosphorus loss to surface run-off is not a significant problem on the SCP due to the flat topography and free-draining sandy soils. The impact from leaching of water-soluble P into the wetlands and river systems is the single greatest factors affecting the long-term amenity and environmental health of coastal waterways (Summers and Weaver 2008).

Phosphorus entering waterways will reduce the economic return from pasture production systems. Fertiliser is generally considered the most expensive input in a farming system and any loss of this commodity can reduce the farmer's financial return on investment (Summers and Weaver 2008). As the price to manufacture, transport and apply P fertiliser increases, the efficiency of applied P fertiliser needs to increase to ensure an economic return. The increase in the price of P fertiliser and the need to increase P use efficiency is often coupled with environmental concerns from P lost to leaching (Simpson *et al.* 2011a). There are several ways to increase P use efficiency which include, soil and tissue analysis to determine the exact rate of P required, and understanding climate and plant requirements. Establishing pasture before applying P fertiliser and often splitting the applications of P fertiliser will also increase P use efficiency. These issues are discussed in more detail in the following sections (see Section 2.4).

2.4 Plant

The main pasture species for livestock grazing underpins the global agricultural meat, milk and wool markets (Ludemann and Smith 2016). The management of plants in the pasture production system is critical in maximising farmer productivity. The management process requires the correct selection of plant species that are adapted to local conditions, livestock (i.e. sheep, cattle) condition and to maximise pasture dry matter production (Nie *et al.* 2004). The species and systems for plant dry matter production vary widely between regions and go from unfertilised rain-fed rangeland systems to intensive irrigated highly fertilised systems. The pasture species used can vary widely and be a combination of both annual and perennial species. The common combination of intensive agricultural systems is a grass (annual ryegrass) and legume (clover) system (Smith and Fennessy 2011). The selection of the correct species is critical to maximise, dry matter growth, productivity, P use efficiency, and be adapted to the environment (Bradshaw 2016).

2.4.1 Typical pastures species of southern Australia

The main pasture species in Temperate or Mediterranean areas of Europe, South America and Australia are a combined mixture of ryegrass and clover. This mixture of species is widely grown for high dry matter yield, high feed nutritional value, and ability to withstand a wide range of grazing conditions (Bryant *et al.* 2016). The composition of Australian pasture has changed over time with the introduction of new species and changes in farming practices to utilise a mixture of legume (clover) and grass (annual ryegrass) pastures (Howieson *et al.* 2000). The south-west Western Australian agro-ecological zones are broadly classified as dry temperate having a Mediterranean wet winters with mild to cool temperatures, and dry, warm to hot summers (Abberton and Marshall 2005; Vertessy 2014).

Clover (*Trifolium* ssp.) is one of the most widely cultivated species for pasture production in Australia (Henzell 2007). Clover was selected for pasture production due to its ability to: adapt to different climatic conditions, ability to regrow after grazing or mowing, high dry matter yield, good nutrition, palatability for livestock, and ability to fix N into the soil to reduce the need for synthetic N fertiliser application (Thomas 1992; Caradus *et al.* 1996). Annual ryegrass (*Lolium rigidum*) is the most common grass pasture species for livestock grazing and silage production due to its high nutrition value. In the 1990's subterranean clover (*Trifolium subterranean*) and annual medics (*Medicago* spp.) dominated annual legume pastures in southern Australia (Nichols *et al.* 2007). Recent research has found that a mixture of species, including clover and ryegrass is required to maximise the pasture dry matter yield and fodder quality (Snaydon 1987; Annicchiarico and Tomasoni 2010). Clover's ability to fix N and ryegrass's requirement for N means they have a symbiotic relationship that increases dry matter yield and forage quality (Thomas 1992; Williams *et al.* 2003; Annicchiarico and Tomasoni 2010). A mixture of the two species also ensures that if a season does not favour one, the other may still produce dry matter for livestock consumption.

Over the last 15 years, several new clover varieties have been developed with traits that incorporate genes originating from the Mediterranean Basin that are better adaptation to Australian climates (Nichols *et al.* 2007). These traits include deeper root systems, protection from false breaks (i.e. germination-inducing rainfall events followed by death from drought), a range of hard seed levels, tolerance to acid soils, and pest and disease resistance (Nichols *et al.* 2007). Ryegrass is one of the most valuable pasture species in the world and plays a major role is Australian pastures (Cunningham *et al.* 1994; Oram and Lodge 2003). Annually over 6 million hectares of ryegrass-based pasture production systems in Australia is grazed for wool, dairy and meat industries. Ryegrass provides the main forage species for the cool season in the subtropics in Australia and is highly productive both regarding herbage and dry matter yield (Lowe *et al.* 1999).

The plant root architecture of clover and ryegrass, particularly root type and surface area, is critical for the plant's ability to uptake P from the soil (Lynch 1995; Somma *et al.* 1998). The plant's root system can significantly affect P uptake and increased root hair length significantly affects the plant dry matter weight due to increased P absorption (Caradus 1981). In pasture production systems, P fertilisers are normally applied using the surface broadcasted method onto the soil to address P nutrient deficiencies. Ryegrass have a fibrous root system that has a greater surface area to capture the surface-applied P (Tisdall and Oades 1979; Fitter and Stickland 1992). A fibrous root system has a greater ability to uptake P generally within the top 30 cm but does reduce the plant's ability to access P at depths below 30 cm (Caradus 1981). Ryegrass has a more fibrous root system than clover and therefore has a greater ability to access P from the soil (Bolan *et al.* 1987). Consequently, clover requires a higher soil P level than ryegrass as its root system has less surface area and cannot obtain the same amount of P in a given volume of soil (Somma *et al.* 1998). Clover and ryegrass are the two main annual species, grown in Australia for pasture production, and with their slightly differing requirement for P, they will be used in this research to determine dry matter yield and plant uptake of P.

2.4.2 Plant nutrient requirements

For plants to grow, thrive and reproduce, they require the ability to capture from the environment both macronutrients (i.e. C, H, O, N, P, K, S, Ca, Mg) and micronutrients (i.e. molybdenum, copper, boron, manganese, iron, chlorine and zinc). Plants also require other microelements such as, sodium, silicon, cobalt, strontium and barium, which are not always essential for plant growth but can aid in livestock health (Fageria 2008). Reduced availability or a deficiency in one of the 16 macro/micro nutrients will limit plant growth and production. This will have consequences even if all the other nutrients are available in adequate amounts (Foster 2015). The macronutrients, carbon, hydrogen and oxygen, are obtained from the atmosphere and water. These three elements combined make up to 95% of dry matter within the plant. The remaining 5% of the nutrients in the dry matter are obtained through the soil via the plant's root system. However, some plants such as legumes also have the ability to obtain and convert N into the plant from the roots. Nitrogen can also be taken up by the plant roots and leaves from applications of liquid fertiliser such as urea ammonia nitrate (Fageria and Baligar 2005; Suter *et al.* 2013). As nutrients, these are used by the plants for growth and then consumed by livestocks or removed for export from the soil; hence it is critical that these nutrients are replaced to maintain optimum plant growth. The rate and type of removal are different between different agriculture production systems and will determine the requirement for, and replacement rate of all these nutrients. For example, a 1 t/ha hay crop comprising 30% clover and 70% ryegrass will remove approximately 35 kg of N, 3.5 kg of P, 25 kg of K and 3 kg of S (Foster 2015).

The size of roots, stems and leaves normally function as interdependent parts of the plant (Caradus 1981). These three systems maintain a dynamic balance in biomass which reflects the relative abundance of above-ground resources (light and CO_2) compared with root-zone resources (i.e. water and nutrients) (Poorter *et al.* 2012). Whole-plant growth rate and various summary measures such as root: shoot ratios are thus an outcome of developmental stage and environmental influences.

2.4.3 Plant uptake of phosphorus

The growth of plant roots will favour colonisation of nutrient-rich areas within a soil (Desnos 2008). The rhizosphere is the narrow region of soil close to the surface that is directly influenced by root secretions and the activity of microorganisms (Giri *et al.* 2005). The areas of the soil that are not part of this surface layer are known as bulk soil. The rhizosphere plays a critical role in nutrient cycling in soil ecosystems (Toal *et al.* 2000). The rhizosphere contains a large volume of bacteria that consume the sloughed-off plant cells, termed rhizodeposition, and the material that is released by plant roots. Plants obtain the majority of core nutrients, especially N, P and S from the rhizosphere (Chen *et al.* 2002). As plants require nutrients to be soluble, it is critical that there is adequate soil moisture within the rhizosphere to allow the plant to access them. The depth of the rhizosphere varies, but nutrients have to remain within this rhizosphere layer to be available to the plant. Nutrients such as N, P, S and iron act as signals that can be received by the plant roots. These nutrients can then trigger molecular mechanisms that modify cell division and cell differentiation processes within the root and have a significant influence on the plant root structure architecture (López-Bucio *et al.* 2003).

Plants access P from the soil via their roots which is then transported to the plant for use where it is required (Cesco *et al.* 2012). Root morphology is critical for the acquisition of P from the soil and root structure can vary widely between pasture plant species (Hill *et al.* 2006). The application of P fertiliser on the soil surface requires rainfall to be dissolved and to infiltrate into the rhizosphere. As the frequency of rainfall events decreases, and depending on the volume of rainfall from these events, the rate of vertical movement of P affects plant growth due to the amount of time that a plant can access any applied P. It is critical that the correct rate of P fertiliser is applied and options investigated to maintain plant available P in the rhizosphere. Plant roots will adapt to nutrient availability in the soil depending on their location and the requirement of the plant (Caradus 1981; Flavel *et al.* 2012). A plant must be adapted (i.e. genetic by environment interaction) to sense and extract nutrients from the rhizosphere to ensure optimum growth. A simple outline of this method where P fertiliser is applied via surface broadcast of plant acquisition of P is outlined in Figure 2.13.

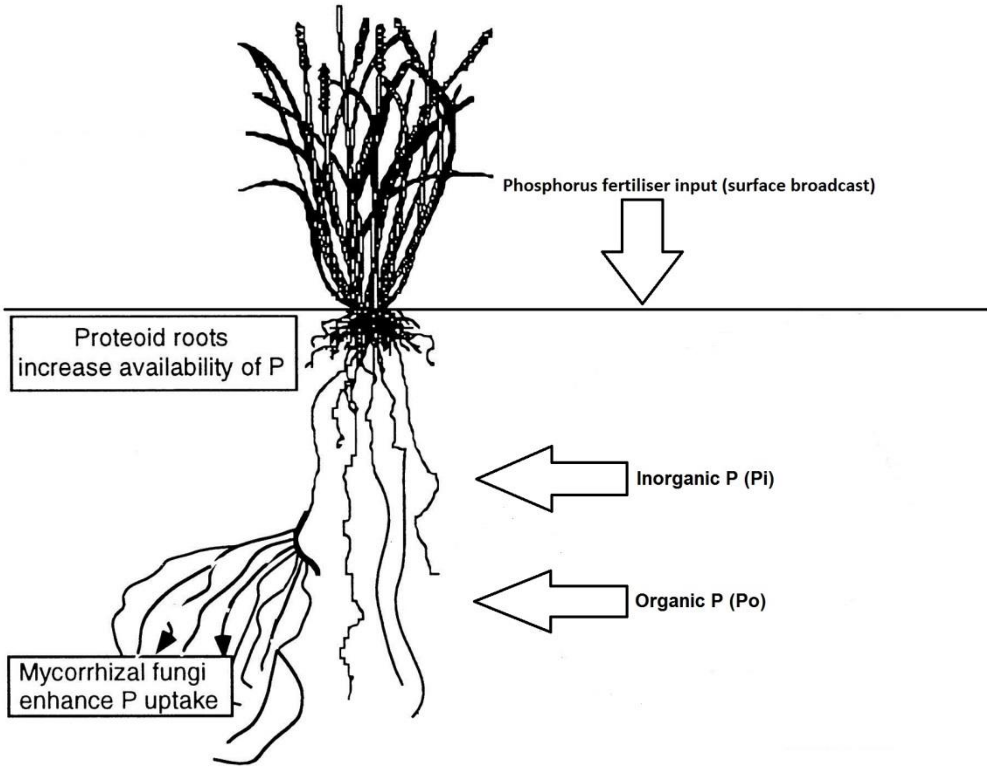


Figure 2.13 Plant acquisition of soil P (modified) (Schachtman *et al.* 1998).

Microbes within the soil can mobilise P by releasing immobile forms of P into soil solution (Sathya *et al.* 2016). The most soluble minerals such as K move through the soil via bulk flow and diffusion. The availability of P within the soil bulk can also influence plant uptake from diffusion. The rate of diffusion of P is slow (10^{-12} to 10^{-15} m^2/s), a higher rate of plant P uptake (10^{-5} to 10^{-8}), can create a zone around the root that is depleted of P (Schachtman *et al.* 1998). The plant availability to access P also depends on root architecture and mycorrhizal fungi while the availability of P is affected by acidification, root exudates from organic acids and other microbial effects (Richardson *et al.* 2009a; Richardson *et al.* 2009b).

The methods that plants use to access and uptake P in the soil vary depending on species, plant root geometry and morphology which all affect maximum P uptake (Schachtman *et al.* 1998; Richardson *et al.* 2011). The root systems that have a high ratio of surface area to volume can effectively explore a larger volume of soil (Lynch 1995). For this reason, mycorrhizae are important for acquiring P, since fungal hyphae generally increase the volume of plant roots (Smith and Read 2008). In some species, root clusters (proteoid roots) are formed in response to the limitation of P. These specialised roots extrude large amounts of organic acid, up to 23% of net photosynthesis. This process of acidification of the surrounding soil and chelate metal ions around the roots results in P mobilisation (Marschner 2012). Phosphorus in soil solution can also rapidly react with other elements in the soil (precipitation) and on the surface of the soil constituents (adsorption) which combine some insoluble compounds (Menezes-Blackburn *et al.* 2016). The term sorption is commonly used to describe precipitation and adsorption events (Bolland and Allen 2003). The replacement of P into soil solution can occur through some sources, including fertiliser application, desorption reactions and mineral dissolution of inorganic P and by the mineralisation of organic P by microorganisms (Sundara *et al.* 2002).

Phosphorus can be very strongly adsorbed by soil particles which restrict movement while P can be transferred over larger distances once in the soil solution. Due to this lack of movement, adsorption of P in soil solution by the plant roots depends on roots intercepting the soil solution as they grow (Bolland *et al.* 1998). The concentration of P in soil solution required for optimum plant growth is about 2 mg/L. However, this can change depending on species and yield potential (Pierzynsk *et al.* 1994). Available P is critical during the early stages of plant development when the root systems are small, and in reduced P situations, this will likely to reduce yield potential (Smith 1967; Bolland and Gilkes 2001).

2.4.4 Measuring phosphorus in plant tissue

Phosphorus is located in all living cells and is involved in a number of critical plant functions, including, photosynthesis, energy transfer, conversion of sugars and starches, movement of nutrients within the plant, and reproductive genetic transfer (Sultenfuss and Doyle 1999). Phosphorus is readily re-translocated from old leaves to new growth and is present in tissue at approximately 0.2% of plant dry matter (Snowball and Robson 1983; Schachtman *et al.* 1998). The recovery rate of applied P fertiliser in clover shoots is relatively low with 30%–35% of P recovered (McLaren *et al.* 2015b).

Plant analysis provides primary information on the nutrient status of plants and can be used as a guide for optimum plant production and nutrient management (Reuter and Robinson 1997). Plant analysis can determine if a nutrient is present and if levels are suitable for plant growth. The critical ranges of P concentrations in clover and ryegrass are between 0.20%–0.40% depending on plant growth stage, with deficiency and toxicity range shown in Figure 2.14 (Haling *et al.* 2016).

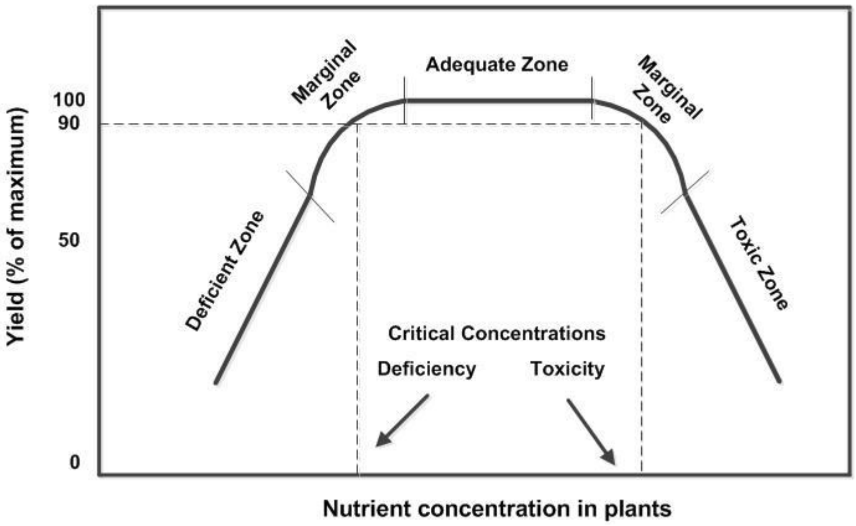


Figure 2.14 Derivation of critical concentrations for nutrient deficiency and toxicity in plants (Reuter and Robinson 1997).

2.4.5 Symptoms of phosphorus deficiency and critical limits

Phosphorus deficiency symptoms can vary depending on factors, such as growth stage and status of other nutrients such as potassium, which result in stunting in plants (Snowball and Robson 1983). Phosphorus deficiency symptoms can be seen in clover with the leaves being smaller and darker green than leaves with adequate P (Snowball and Robson 1983). Phosphorus deficiency in ryegrass generally appears on the oldest leaves first, with darker green leaves, dead or brown leaf tips with curled leaves and stunted growth (Havilah *et al.* 2005). The critical concentration of P for a range for ryegrass and clover at different growth stages is shown in Table 2.8.

Table 2.8 Critical phosphorus concentration in tissue analysis (Reuter and Robinson 1997). Perennial ryegrass is shown as no values for annual ryegrass is available from this source.

Pasture species	Growth stage	Critical P range (%)
Subterranean clover (*Trifolium subterranean*)	Young open leaf Whole tops	0.30–0.40 0.28–0.32
Perennial ryegrass (*Lolium perenne*)	Young open leaf Whole tops	0.20–0.28 0.20–0.25

Phosphorus toxicity in plants is indicated by interveinal chlorosis in younger leaves and may look like iron deficiency. The leaves will have symptoms of tip dieback and necrosis in vulnerable species (Bhatti and Loneragan 1970). The plants may also have interveinal necrosis, marginal scorch and shedding of their older growth (Reuter and Robinson 1997).

2.5 Phosphorus (nutrients)

Australian agriculture requires the use of fertilisers to increase and improve crop and pasture production as defined by Speirs *et al.* (2013), with this due to inherently low fertility and concentrations of both available P and total P in Australian soils (Wild 1957; Beadle 1962; McLaughlin *et al.* 2011). Generally Australian soils have 40% less P than the United Kingdom soils and up to 50% less than soil located in USA (Foster 2015). The use of SSP has rapidly increased between 1920 and the 1970s Donald and Williams (1954) up to about 480 kt P per year and then dropped to the current usage 300–500 kt per year (McLaughlin *et al.* 1992). Pasture production in the south-west of Western Australia involves using the 4Rs principle, right P source, applied at the right rate, at the right time and to the right place ((IPNI 2016). The application rate of P fertiliser to pasture is generally based on a number of factors including P buffering index (PBI) as defined by (Sounness 2008; Moody *et al.* 2013), soil analysis Colwell (1965), pasture species, and targeted dry matter yield.

Once a target dry matter yield has been established, the application of P fertiliser pasture production systems is generally applied through the broadcast method (Khairo *et al.* 2009; Smith *et al.* 2016). This method is used because the majority of pastures paddocks are self-sown and can be re-sown periodically to improve pasture species or composition. Pasture fertilisers are applied by the broadcast method because of the relative quantity of SSP and that it will not pass through modern air-seeders due to variation in particle size and low granule strength. For these reasons, the broadcast method is used even through drilled P is more effective than surface broadcast applied P (Rudd and Barrow 1973).

2.5.1 Development of phosphorus fertilisers

Phosphorus was identified as an essential element for plant growth as early as 1830, when bone meal and guano treated with sulphuric acid (H_2SO_4) was used to increase the solubility and plant availability of P (Foth and Ellis 1988). The chemistry of the solubilising action of acids on natural P was discovered around 1796 (Agriculture 1964). Modern agriculture uses P from rock phosphate which is of marine origin and is mined and manufactured into chemical fertilisers (Johnston 1994). The principal mineral from marine formed rock phosphate is Apatite, which accounts for at least 95% of P found in igneous rock. Phosphorus for agriculture can also be obtained from recycling, including biosolids from human waste (Pritchard 2005). Use of P sourced from manures and organic sources to improve crop growth dates back to approximately 1000BC. The history, development, mining, manufacture, chemistry and application of artificial fertilisers has not changed much since the 1920s, and this is summarised by (Parrish and Ogilvie 1927; Johnston 1994).

The main chemical fertiliser currently used in mixed pasture systems is single superphosphate (SSP), which is derived from rock phosphate, due to relatively low-cost manufacture, and is suitable for plant nutrition. The chemical analysis of SSP varies depending on where the rock phosphate is sourced and the method of manufacture (Darlow 2009). Single superphosphate manufactured in Western Australia has a typical analysis of 9.1% phosphorus, 10.5% sulphur and 20% calcium (Darlow 2009). The manufacturing process by which rock phosphate is processed into single superphosphate is outlined below in Table 2.9.

a. Phosphate rocks are blended and crushed to a fine powder (rock dust).
b. The rock dust is mixed with sulphuric acid and water to form a thick slurry.
c. The slurry is heated to approximately 120°C.
d. The slurry sets into a cake in 30 to 45 minutes.
e. The cake is mechanically broken into fine pellets.
f. The fine pellets are conveyed to a granulating plant where they are rolled into granules, sized, and sent to storage where it matures prior to dispatch.

Table 2.9 The chemical reaction of the manufacture of single superphosphate (Darlow 2009).

Rock phosphate		Single superphosphate
$Ca_3 (PO_4)_2 + 2H_2SO_4 + H_2O$	$\longrightarrow$	$Ca (H_2PO_4)_2 H_2O + 2CaSO_4$

2.5.2 Phosphate forms

Phosphorus derived from rock phosphate is made up of three types of phosphate with the ratio of these types determined by the quality of sulphuric acid applied as defined by Mclean and Wheeler (1964) and the purity of the rock phosphate (Parrish and Ogilvie 1939). The chemical form and analysis of these three types of phosphate contained within SSP are outlined in Table 2.10. The fertiliser manufacturing process from rock phosphate to SSP cannot completely convert all phosphate to a single form and consequently, there is always a percentage of all three forms in any fertiliser produced. Single superphosphate has always been designed to have the maximum amount of monobasic calcium phosphate as this form is very soluble in water (Kao 2015). Monobasic calcium phosphate is readily used by plants (Wild 1988).

Table 2.10 Chemical form, solubility and chemical structure of phosphate fertiliser derived from rock phosphate.

Chemical forms	Solubility	Chemical analysis
Monobasic calcium phosphate	Water-soluble	$Ca(H_2PO_4)_2\ H_2O$
Dibasic calcium phosphate	Citrate-soluble	$CaHPO_4\ 2H_2O$
Tribasic calcium phosphate	Citrate-insoluble	$Ca_3(PO_4)_2$

The three forms of phosphate present in fertilisers derived from rock phosphate with their solubilities and their chemical analysis. Monobasic calcium phosphate is the most soluble, with the solubility reducing as the ratio of calcium to phosphorus atoms increases.

2.5.3 Manufacturing of low water-soluble superphosphate

The manufacture of low water-soluble superphosphate (LWSSP) is similar to that of SSP with the process described by (Parrish and Ogilvie 1939; Agriculture 1964; Darlow 2009) and only requires lime-sand to alter the process (Smith 2015). As the SSP is manufactured, limesand is added to the material in a controlled way to maintain the ratio of SSP to lime-sand. A disintegrator provides the mixing to ensure homogenisation of the material and then it is granulated and screened as per the normal process. The resulting LWSSP is hot, damp and irregular in size. The granulation system then uses a disintegrator to break up the material into regular-sized, fine particles, which is transferred into the granulation drum where water is sprayed to re-granulate the LWSSP to the required size range. This material is screened, and the correctly sized material is delivered to a storage shed and under/oversized material is processed again (Smith 2015).

Water is critical to the reversion process due to the way that SSP and lime-sand react, it generates heat and slowly dries out. The application of water has to be controlled to provide sufficient water for the reaction and granulation but not too much as to make the material too wet and unstable. The quality of the lime-sand is critical, with the smallest particle size and highest neutralising value preferable (Riley 2011). Cumming Smith British Petroleum (CSBP) Limited uses lime-sand sourced from Lancelin, Western Australia, in the manufacture of LWSSP due to its high neutralising value. The rate of limesand application was determined by laboratory experimentation by CSBP. To reach 40% water-soluble P, approximately 18.5% of limesand is needed, however, it is usually over-supplied (to account for process inconsistencies) at 20% which gives 33 to 35% water-soluble P (Smith 2015). The typical composition of SSP and LWSSP is outlined in Table 2.11.

Table 2.11 Percentage composition and phosphorus analysis of two superphosphate fertilisers.

	SSP	LWSSP
Total P (%)	9.1	8.3
Monobasic calcium phosphate[A]	7.8 (86)	2.9 (35)
Dibasic calcium phosphate[A]	0.8 (9)	3.7 (45)
Tribasic calcium phosphate[A]	0.5 (5)	1.7 (20)

Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP). The percentage of each form of phosphate (within the brackets).

[A] Measured by standard (AOAC 1975).

Adding limesand has a number of implications for SSP:

1) Limesand consumes all the free acid in the product and hence stops the maturation process. The amount of acid-insoluble P remains fixed and does not change.
2) A high rate of limesand reduces fertiliser granule strength and fertiliser quality.
3) The reversion process is slow and can take up to six weeks for it to complete. The rate of reversion is related to the amount of moisture in the product, which makes the manufacturing process important.

The reversion process needs water and a base (e.g. limesand) to convert the MCP into the DCP to lower the water-soluble component of superphosphate. The degree of reversion is dictated by the amount of basic material that is added, with the chemical equation outlined in Equation 2.1:

$$Ca\,(H_2PO_4)_2 + H_2O = Ca\,(HPO_4) + H_3PO_4$$

$$H_3PO_4 + CaCO_3 = CaHPO_4 + CO_2 + H_2O$$

Equation 2.1 The chemical equation to create low water-soluble superphosphate from single superphosphate (Smith 2015).

2.5.4 Phosphorus recommendation models

Applying the correct rate of P is critical for maximising pasture dry matter yield and minimising over-application of P fertilisers (Summers and McLaughlin 1996). Using soil and tissue analyses, any nutrients or soil properties limiting dry matter yield can be determined and overcome. Determining the correct rate of P to apply is generally conducted through using a fertiliser recommendation model that is based on glasshouse and field experiment data (Sinclair and Johnstone 1995). The rate of P required is determined by inputs such as: soil analysis, phosphorus binding index, Colwell P, pasture species, and the dry matter yield target (Sinclair *et al.* 1993; Ratkowsky *et al.* 1997; Cullen *et al.* 2008). A number of industry and commercial models (e.g. Nulogic by CSBP) have been developed to provide P application recommendation rates for better fertiliser decisions for pastures (Gourley *et al.* 2007; Dowling 2015).

2.6 Management of phosphorus fertilisers

Environmental and climatic conditions must be matched with the management of P fertiliser to achieve the maximum dry matter production (McLaren *et al.* 2015a). It is also essential that soil analysis is used to determine the amount of P fertilisers that is required so the soil properties can then be compared to the known response curve and the optimum economical response rate determined. The cost of soil analysis to determine the optimum rate of P fertiliser can be expensive. Allen *et al.* (2001) compared two methods to establish a more cost-effective alternative to replacing the expensive PRI sorption curve method. This improved method has allowed more soil analyses to be undertaken at a reduced cost and time (Allen *et al.* 2001).

Inorganic P fertilisers are particularly important in Australia with its ancient nutrient depleted soils (Moore 2004). Australian soils have relatively low P reserves and a limited capacity to supply P to plants over an extended number of seasons in agricultural production systems. Therefore, it is a common practice to apply annual applications of P fertilisers to the soil to ensure P is not limiting and that P is maintained (Ozanne and Shaw 1967; McLaren *et al.* 2015a).

The problem of P loss from leaching after applying fertiliser on lighter soil types is well understood, and a considerable amount of research has been conducted to mitigate this problem (Simpson *et al.* 2011b). These methods can be split into four categories: management methods, changing the physical properties of the soil, coating agents onto the fertiliser, and manipulating the physical and chemical properties of the fertiliser. These methods are discussed in the following sections.

2.6.1 Management methods

The simplest management method to minimise P leaching is to match P application with the plant's specific requirements. A soil analysis will determine the required application rate of P fertiliser, and this requirement can be matched to the pasture species being grown (Chisholm and Blair 1988). This method is often associated with multiple applications of high water-soluble superphosphate, such as SSP (Bush and Austin 2001). It requires the application of enough P to ensure early plant growth and root establishment, and a number of subsequent fertiliser applications throughout the growing season. The subsequent applications are based on the plant's requirements and are normally applied post-grazing for a pasture system (Bush and Austin 2001). This method reduces the risk of P loss to leaching by minimising the P applied each time according to plant requirements. This method can also be used to a lesser extent for applications of other nutrients, such as N to reduce leaching (Di and Cameron 2005).

This ‘drip feeding’ approach has a number of limitations, the workload for farmers and the cost of fertiliser spreading increases as a function of the number of applications. Access to the land may be limiting due to low trafficability from winter rainfall that can stop farmers from using tractors and spreaders. Multiple P fertiliser applications, if not conducted at the appropriate time, can limit production if P becomes deficient (Bush and Austin 2001; Burkitt *et al.* 2011). To reduce P leaching, these fertiliser applications need to account for landscape topography and buffer zones around water systems (Cox *et al.* 2007).

The combination of soil analysis using Colwell and PBI single point absorption analysis allows the accurate prediction of P fertiliser application rate to achieve optimum growth or yield response. The application of P fertiliser should take into account the two methods and a number of other factors including, the type of P fertiliser, rainfall, climate, plant species and required growth or plant yield, the number of samples and location of the sample area (Bolland 1987). The time of year that soil is collected can influence the results due to the amount of extractable P depending on seasonal condition, such as summer rainfall and temperature before sample collection (Moore 2004).

2.6.2 Changing the physical properties of the soil

The physical property of soil and the ability to retain applied P is quantifiable with measurement of PRI and PBI. The application of the material in the soil to reduce the solubility of P has been investigated at a number of locations globally where soil P is at least adequate for the requirement of plant growth (Seshadri *et al.* 2013). In the USA, a coal combustion byproduct was applied to the soil and it was successful in reducing soil P to a level that reduced loss to the environment while maintaining an adequate supply for plant production (Stout *et al.* 1998; Johnson *et al.* 2011).

Bauxite residue is an alkaline, finely crushed by-product produced in large quantities by the alumina industry and has a high ability to retain P. A solution for safe environmental disposal of bauxite residue is required with a number of possible options proposed by CSIRO (Klauber *et al.* 2009). Summers *et al.* (1996b) investigated the effect of bauxite residue on P leaching on sandy soils over a 12-month period with simulated rainfall and climatic conditions of those found on the SCP for a five-year period. Bauxite residue was applied to the soil surface of bleached grey sands, with and without gypsum at rates from 5 to 80 t/ha and the leachate was analysed. It was determined that the economic optimum rate of bauxite application of 5 to 10 t/ha which reduced P leaching rates for at least five years after application (Summers *et al.* 1996b). The reduction in P leaching achieved from applying bauxite residue was further investigated to determine if this reduction would increase pasture production and to evaluate if heavy metals would be taken up by plants (Summers *et al.* 1996a). The bauxite residue did not increase levels of heavy metals in plant tissue, hay or soil. The application of bauxite residue did, however, increase P retention in the soil and pasture production, but it was not widely adopted due to practical and community concerns. The community concerns included the cost of transport and spreading, and the levels of radioactivity emitted from bauxite residue since it contains amounts of radioactive thorium, uranium and potassium. Summers *et al.* (1993b) It was determined that if the site were 100% occupied for a year (365 days), a rate of 1500 t/ha of bauxite residue would emit unacceptable levels of radioactivity for human occupation.

Industry by-product fly ash and biochar have potential to be used as a soil ameliorant to reduce P leaching, and it was investigated at a number of locations globally (Pathan *et al.* 2002; Pathan *et al.* 2003; Buecker *et al.* 2016). Biochar has been shown to reduce the loss of P and K to the environment while increasing the pH of leachate when applied to Australian soils (Buecker *et al.* 2016). Fly-Ash applied to sandy soil significantly increased plant available P to rice when grown in South Korea at rates up to 120 Mg/ha^{-1} (Lee *et al.* 2007). In Western Australia, fly ash is a by-product of power generation and was obtained from the Kwinana power station, where approximately 50,000 tonnes are produced annually (Summers *et al.* 1998). Fly ash contains P as unweathered (409.9 ± 3.1 mg/kg) and weathered (92.5 ± 3.1 mg/kg) compounds. Fly ash was applied to “Karrakatta sand” (Brown Podsol) sourced from the SCP in a leaching column experiment at 5, 10 and 20% weight/weight (McArthur and Bartle 1980; Pathan *et al.* 2002). This result indicated that fly ash could be used as a soil ameliorant to reduce the amount of P leaching on the SCP. However it was not widely adopted owing to the cost of transport and application to the soil.

2.6.3 Coating of phosphorus fertilisers

Coating bauxite residue onto the surface of SSP was investigated by (Summers *et al.* 1999a). It was concluded that a coating of 30% reduced P leaching by half, and increased P uptake and plant dry matter yield. From this experiment a coating of 25% bauxite residue was selected for a field experiment at Demark, Western Australia on a humic aquic podosol soil as defined by Isbell (1996), over a three years period with applications of bauxite residue coated and SSP applied every year Coating of SSP with bauxite residue reduced P loss to leaching and increased dry matter yield, however this method was not widely adopted due to high cost of integration and the infrastructure to manufacture it (Klauber *et al.* 2009).

Aiming to increase P use efficiency, plant uptake and yield through the controlled release of P to match plant requirements, Pauly *et al.* (2002) studied the application of a polymer coating to the fertiliser granule. The results indicated that the thin-coated released P more slowly and increased plant growth at early stages than control uncoated di-ammonium phosphate. The thicker-coated polymer released P even more slowly and at later growth stages (Pauly *et al.* 2002). This relationship between the thickness of coating and number of holes means that the relative amount of P released could be controlled and matched to plants requirements/environmental conditions to reduce P leaching. Although the study did not investigate the properties for a reduction in leaching, it can be inferred that this technology could be applied to SSP to slow the loss of P to leaching due to it increased plant uptake and P use efficiency. This polymer technology has not been further investigated but merits further investigation.

2.6.4 Manipulating physical and chemical properties

The relationship between P fertiliser particle size (i.e. surface area) and the effect of P solubility was investigated by (Owens *et al.* 1955; Williams and Lipsett 1968) in a glasshouse study using clover grown on four soil types. The larger a fertiliser granule, the less soluble it is (Williams and Lipsett 1968). Owens *et al.* (1955) found that as granule size increases or an increase in water-soluble P, the distance of P migration was reduced (see Table 2.12).

Table 2.12 Relationship between the water-soluble phosphorus content of fertiliser granules and the migration of phosphorus in soil adjacent to the granules[A] (Owens *et al.* 1955).

Water-soluble fraction of phosphorus fertiliser	Specific activity of rings of soil concentric to fertiliser granule[B] Counts per minute[C]			
%	0 to 3.5 mm	3.5 to 6.0 mm	6.0 to 8.5 mm	8.5 to 11.5 mm
2 to 3	153	116	*	*
8 to 10	1355	311	62	*
18 to 20	1130	1004	20	*
28 to 30	2530	1512	137	*
40 to 45	3499	2478	844	225
85 to 90	4288	3639	1391	475

[A] After 7 day incubation period in Hillsdale sandy loam soil containing 11.5% moisture.

[B] 4 to 6 mesh granules of 12–12–12 fertiliser.

[C] Activity measurements represent the mean of 3 replicates.

The process of granulating SSP is a relatively simple technology for most manufacturers of fertiliser and granulated fertiliser and is commonly used for growing broadacre crops, such as wheat, barley and canola. However, the effectiveness of granulated SSP is not often researched since farmers commonly use more than one fertiliser through air-seeders for cropping, thereby reducing the effectiveness of granulation. As rock phosphate is the base ingredient for the production of SSP fertilisers and the relative acidic nature of Australia soils, limited amounts of rock phosphate is dissolved when applied to these soils. A number of investigations have examined rock phosphate as a source of P for plant growth (Bolland *et al.* 1986; Hughes and Gilkes 1986; Weatherley *et al.* 1988; Bolan *et al.* 1993). Phosphorus within rock phosphate is present in a very insoluble form.

Manipulating the chemical composition of rock phosphate to increase P use efficiency is well known (Parrish and Ogilvie 1927, 1939; Bolan *et al.* 1990; Darlow 2009; Yang *et al.* 2012b). Since plants require access to water-soluble P for uptake, most of the P fertilisers are designed to have the maximum percentage of P available in a highly soluble form. Several studies investigated the application of rock phosphate, partially acidified rock phosphate, or rock phosphate blended with water-soluble fertiliser to reduce leaching and increase plant dry matter yield (Mclean and Wheeler 1964; Bolland and Bowden 1982; Bolland *et al.* 1986; Hughes and Gilkes 1986; Bolland *et al.* 1987; Bolland *et al.* 1988; Weatherley *et al.* 1988;

Deeley 1989; Bolland 1994; Bolland *et al.* 1995; Babare *et al.* 1997a; Simpson 1997; Prochnow *et al.* 2008). In 1997, Bolland *et al.* (1997) reviewed all of the rock phosphate research which indicated that rock phosphate fertilisers are not an economical substitute for SSP for most agricultural production systems in Australia. This study did acknowledge that limited research has been conducted on the availability of P to plants from rock phosphate under favourable conditions, that have high rainfall, acidic soils and highly reactive rock phosphate (Bolland *et al.* 1986; Bolland *et al.* 1997).

2.7 Summary from literature review

The literature suggests that there is limited research on manipulating the chemical properties of SSP to reduce P loss to the environment while maintaining available P for plant growth in pasture systems (Yeates and Clarke 1993; Yang *et al.* 2012b). The literature review concludes that it should be possible to determine the relative effectiveness of an LWSSP fertiliser compared to SSP, as a source of P to reduce P leaching and maintain pasture production systems (Rodríguez *et al.* 1996).

There is a distinct lack of information about the effectiveness of LWSSP as a source of P for plant growth. Extrapolating from published reports, it is expected that LWSSP would be as effective as SSP based on its chemistry under high rainfall conditions on soils with a low PBI. It is expected that manipulating the phosphate chemistry contained within SSP, that will allow the plant to assimilate P from MCP that enters into the P solution pool within the soil. Since some soils on the SCP have a relatively low ability to adsorb P and results in a small solution pool, it is proposed that by increasing the percentage of DCP within SSP that the SSP will dissolve at a slower rate and enter the active pool. This modification will increase the amount of P available in the solution pool over a longer period. The change in SSP to make LWSSP ratios of MCP and DCP was based upon a number of issues that include, proposed government legalisation limiting the water soluble content of P fertilisers to 40% or less, the physical chemistry process to convert the remaining phosphate to DCP, and the granular strength of the LWSSP fertiliser. The percentage of MCP within SSP can be decreased, and the percentage of DCP increased to make LWSSP, but the amount of TCP cannot be decreased as it is a by-product of the chemical process. With all these factors in mind, it was decided that the chemistry of LWSSP with a MCP proportion of 40% was correct for this research.

Therefore, the three experimental chapters in this thesis further investigate the characteristics of LWSSP as a fertiliser for pasture production systems on the SCP in south-west, Western Australia. While the research will focus on the application of LWSSP, the information gained from modifying the types of P can be transferred to many other locations globally to reduce the impact of applied P. This research will focus on the, soil, plant growth, leaching, environment and soil chemistry in order to understand the complex interaction that takes place between these factors and P.

CHAPTER 3 GENERAL MATERIALS AND METHODS

3.1 Introduction

This chapter presents the materials and methods that relate to all chapters, details specific to individual experiments are given in the relevant chapter. Section 3.2 contains additional site and soil descriptions, Section 3.7 describes the experimental design and treatment structure and Section 3.8 to 3.10 describes the data collection, experimental equipment and statistical analyses used for each experiment. Two glasshouse experiments, two leaching column experiments and two field experiments were conducted as part of this PhD research.

The first glasshouse experiment was established in June 2014 at the South Perth office of the Department of Agriculture and Food, Western Australia Figure 3.1 to investigate solubility of P, SSP, LWSSP, MCP, DCP and TCP and their effect on plant growth. The second glasshouse experiment was established in October 2012 at the South Perth office of the Department of Agriculture and Food, Western Australia to investigate P availability from LWSSP and SSP using three soil types to evaluate soil P retention, rate and amount of P leaching, plant dry matter yield and P concentration in plant tissue. Section 3.2 contains additional site and soil details, and this experiment is described in full in Chapter 5. The leaching column experiments were established at CSBP Limited, Kwinana, Western Australia to investigate P solubility of SSP, LWSSP, MCP, DCP and TCP under simulated rainfall conditions Figure 3.2. The experiment was conducted within the CSBP field research equipment shed between mid-January to late February 2014. Section 3.2 contains additional site details, and this experiment is described in full in Chapter 9.

The field experiments were established in May 2009 at two locations on the SCP. Site 1 was north of Pinjarra and site 2 east of Serpentine Western Australia Figure 3.3. Section 3.2 contains the site and soil descriptions and Chapter 6 present the results. The field experiment sites were used to evaluate the pasture response to LWSSP, compared to SSP. Annual clover and ryegrass were used as the indicative pasture species because they represent the pasture species grown in this area (Snaydon 1987). The field sites were selected for the following reasons: 1) They were both located on the SCP; 2) both had a PBI of less than 15; 3) the sites would both be in pasture for three years with grazing stock available; 4) both sites had low initial Colwell P levels; 5) both sites were easily accessible and not prone to waterlogging; and 6) and hence were susceptible to leaching of P and were located on properties with farmer support for this project.

3.2 Site locations and soil descriptions

3.2.1 Glasshouse experiments

Glasshouse experiment 1 was located in building 27 and glasshouse experiment 2 was located in building 21 as shown in Figure 3.1.

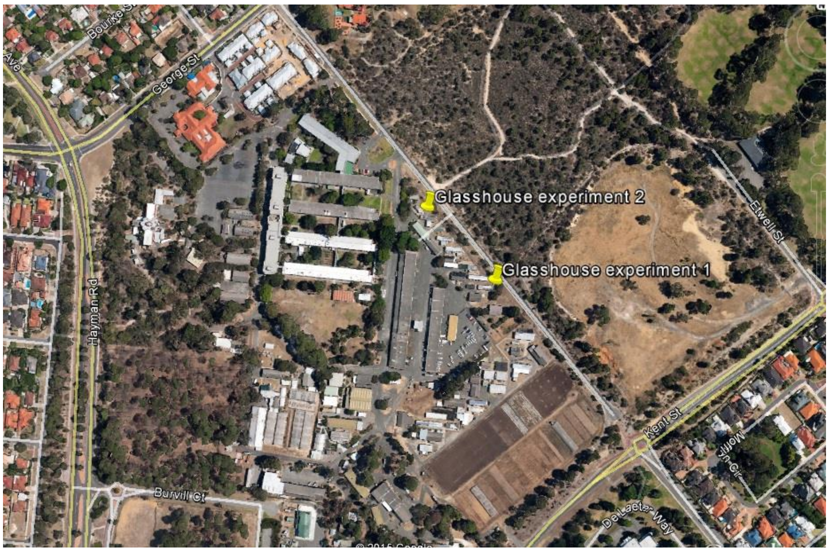


Figure 3.1 Location of the two glasshouse experiments areas at the South Perth office of the Department of Agriculture and Food (Earth 2015c).

3.2.2 Leaching column experiments

The leaching column experiments were located at CSBP Limited, Kwinana, Western Australia, within the field research equipment shed and used existing infrastructure of columns and benches (see Figure 3.2).

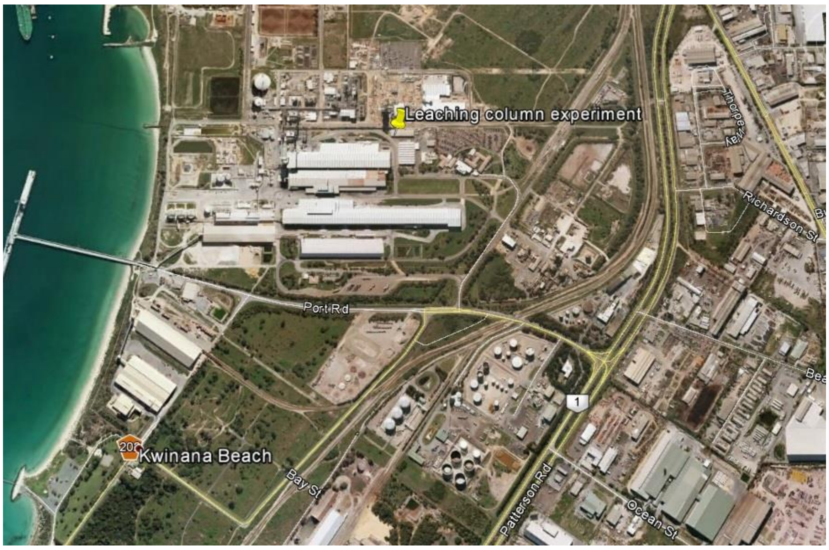


Figure 3.2 Location of the leaching column experiment at CSBP Limited, Kwinana Western Australia (Earth 2015a).

3.2.3 Soil collection sites

The three soil types for glasshouse experiment two as described in Chapter 5 were collected from three locations on the SCP that ranged in the soil's ability to absorb P (see Figure 3.3). These soils were selected because: 1) they had a known PBI and represented the soil types typical of the SCP; 2) the light soil was from field site 2 and would provide a comparison with field experiment; and 3) The researcher had farmer permission and support for the collection of the soil from these locations. The soils are classified as light, medium and heavy for the purpose of the experiment. The light soil type was collected from experiment site 2, east of Serpentine, Western Australia (see Figure 3.4). The medium soil type was collected 8.5 km on a bearing of 232° from Pinjarra, Western Australia, and the heavy soil type was collected 16.5 km on a bearing of 176° from Pinjarra.

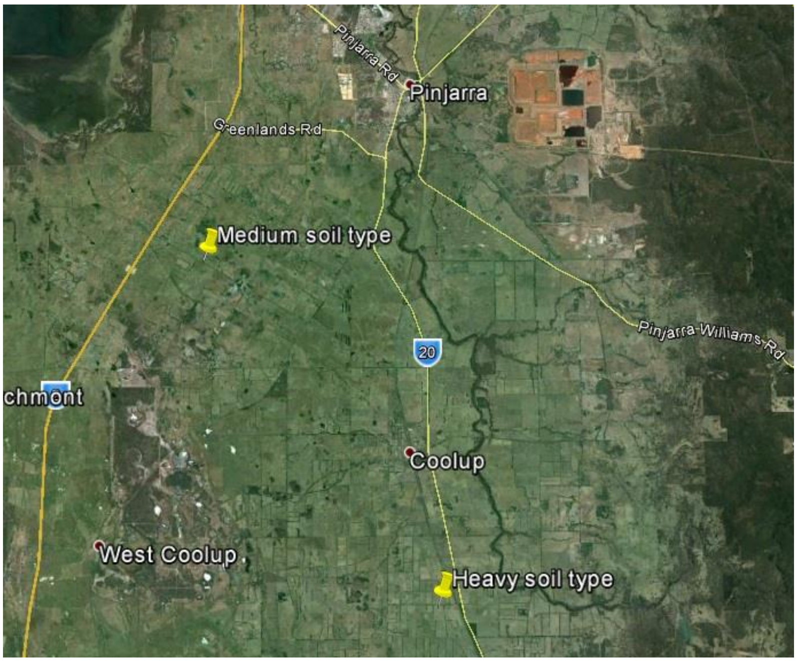


Figure 3.3 Location of the medium soil type longitude (south): 32° 47′ 930″ latitude (east): 115° 53′ 642″ and heavy soil type longitude (south): 32° 40′ 586″ latitude (east): 115° 48′ 062″ collection sites (Earth 2015d).

The two field experimental sites were located on cattle grazing land and managed according to conventional high rainfall, dryland, temperate conditions. Site 1, Thompsons, is a flat open paddock located approximately 10 km on a bearing of 347° from Pinjarra and 1.4 km east of Patterson Road. Site 2, Evans, is a small, flat open paddock that is fenced to allow cell grazing of the pasture by cattle. The site is approximately 4 km on a bearing of 256° from Serpentine. Before establishing the field experiments in mid-May 2009, both sites had 2.5 t/ha of limesand applied to increase soil pH as both sites initial soil test indicated that they had a pH below 4.6 ($CaCl_2$) at 0–10 cm (Riley 2011) (see Table 3.1).

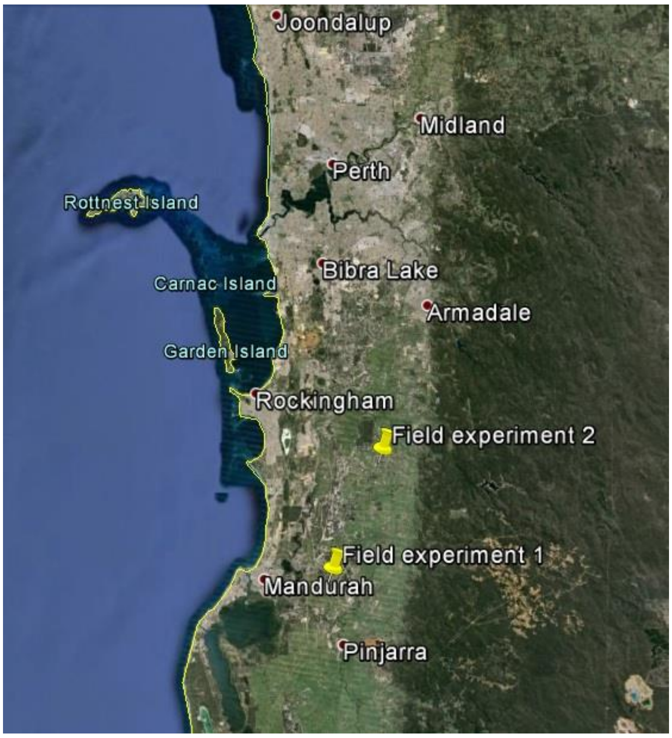


Figure 3.4 Location of the two field experiment sites. The coordinates: field experiment site 1 longitude (south): 32° 32′ 323″ latitude (east): 115° 50′ 596″ and field experiment site 2 (longitude (south): 32° 22′ 264″ latitude (east): 115° 55′ 583″ (Earth 2015b).

3.2.4 Soil characteristics

The physical and chemical properties of the three soils used in glasshouse experiment 2 and the field experiment sites are given in Table 3.2. The three soils used in glasshouse experiment 2 had different PBI levels of 8.9 (light soil type), 16.4 (medium soil type) and 121.3 (heavy soil type) with pH (1:5 $CaCl_2$) all less than 5.0.

The soils at the field experiment sites had a low ability to retain P, with PBI levels of 10.6–15 at 0–30 cm depth. The soil acidity at both sites was quite high, with a pH (1:5 $CaCl_2$) less than 4.6. The soil types had increasing levels of P (Colwell) from 10 mg/kg in the light soil type, 27 mg/kg in medium soil type and 70 mg/kg in the heavy soil type.

Both field experiment sites had low levels of available P (Colwell) levels at less than 12 mg/kg, with the average of samples recording 2–4 mg/kg. Levels of available potassium (K) (Colwell) were low, with 45 mg/kg at site 1, and 27 mg/kg at site 2, both levels declined to 15 mg/kg at 10–30 cm. Sulphur and N levels were also low, with sulphur ranging from 1.2 to 6 mg/kg and nitrate-N ranging between 3 to 15 mg/kg (Foth and Ellis 1988). Glasshouse experiment one was conducted using perlite and the properties of this material are outlined in Table 3.3.

Field experiment site 1, 2 and the light soil from glasshouse experiment 2 are broadly classified as podzols (humus). The medium soil from glasshouse experiment 2 was broadly classified as a zanthic (ferrosol) and the heavy soil type as a chromic (vertisoil) (McArthur 1991).

Table 3.1 General physical and chemical characteristics (dry soil basis) of all the soils used.

Sample identification	Sample (year)	Depth (cm)	pH (1:5 $CaCl_2$)	PBI	Sand (%)	Silt (%)	Clay (%)	Texture	Soil colour
Field experiment	2009	0–10	4.3	14.6	ND	ND	ND	Loamy sand	Grey
Site 1	2009	10–20	3.8	13.6	ND	ND	ND	Loamy sand	Dark grey
	2009	20–30	3.8	14.7	ND	ND	ND	Loamy sand	Dark grey
Field experiment	2009	0–10	4.6	10.6	ND	ND	ND	Loamy sand	Grey
Site 2	2009	10–20	4.3	ND	ND	ND	ND	Loamy sand	Light grey
	2009	20–30	4.0	15.0	ND	ND	ND	Loamy sand	Light grey
Glasshouse experiment light soil	2012	0–10	4.6	8.9	96.09	< 0.01	3.91	Loamy sand	Light grey
Glasshouse experiment medium soil	2012	0–10	4.5	16.4	92.96	2.02	5.01	Sandy loam	Dark grey
Glasshouse experiment heavy soil	2012	0–10	4.9	121.3	59.70	7.24	35.10	Clay	Grey brown

ND – Data not recorded, phosphorus buffering index (PBI) (Allen and Jeffery 1990b).

Table 3.2 Nutrient concentrations (dry soil basis) for all soils used before the lime-sand was added.

Sample identification	Sample (Year)	Depth (cm)	P (Colwell) (mg/kg)	P (total) (mg/kg)	N (NO_3^-) (mg/kg)	K (Colwell) (mg/kg)	S (KCl-40) (mg/kg)	OC (%)
Field experiment	2009	0–10	3	ND	15	27	6	3.57
Site 1	2009	10–20	2	ND	7	15	2.8	3.22
	2009	20–30	2	ND	3	15	1.2	1.07
Field experiment	2009	0–10	12	ND	14	45	5.8	2.17
Site 2	2009	10–20	4	ND	3	15	1.3	0.48
	2009	20–30	3	ND	6	15	2.4	1.62
Glasshouse experiment light soil	2012	0–10	10	36	4	23	2.3	0.82
Glasshouse experiment medium soil	2012	0–10	23	100	42	83	7.1	2.13
Glasshouse experiment heavy soil	2012	0–10	70	478	144	312	24.3	3.09

ND – Data not recorded, phosphorus (P) (Colwell 1965; Rayment and Lyons 2011), nitrogen (N) (Rayment and Lyons 2011), potassium (K) (Colwell 1965), sulphur (S) (Blair *et al.* 1991) and organic carbon (OC) (Walkley and Black 1934; Rayment and Lyons 2011).

Table 3.3 Perlite analysis.

P (Colwell) (mg/kg)	N (Nitrate) (mg/kg)	K (Colwell) (mg/kg)	S (mg/kg)	OC (%)	EC (dS/cm)	pH (1:5 $CaCl_2$)	PBI
4	< 1	160	5.5	0.13	0.042	6.7	5.4

Phosphorus (P) (Colwell 1965; Rayment and Lyons 2011), nitrogen (N) (Rayment and Lyons 2011), potassium (K) (Colwell 1965), sulphur (S) (Blair *et al.* 1991), organic carbon (OC) (Walkley and Black 1934; Rayment and Lyons 2011), electric conductivity (EC) (Rhoades *et al.* 1999), pH (Sparks *et al.* 1996) and phosphorus buffering index (PBI) (Allen and Jeffery 1990b).

3.3 Soil sampling and analysis

3.3.1 Sampling and characterisation

At the soil collection sites, the surface layer of organic matter was removed and the top 0–10 cm of soil was removed from an area approximately 5 m^2 and placed into 50 kg polypropylene bags. The soil was then transported to CSBP Limited field research shed where they were then placed on a large tarpaulin and allowed to dry (Plate 3.1). The light and medium soils were then sieved through a 2.2 mm screen, and the heavy soil was transported to the CSBP Limited Laboratories in Bibra Lake, Western Australia. The heavy soil was ground and sieved using a 2 mm screen. Following this the soil was placed into three 40 kg bags and a single representative 2 kg sample of each collected from each bag for each soil type. The nine soil samples were placed in a labelled sealed bag and submitted to CSBP Limited Laboratories, which is an Australasian Soil and Plant Analysis Council accredited laboratory for analysis.

Plate 3.1 Soils used in the glasshouse experiment. Heavy soil type (left), medium soil type (centre), light soil type (right).

To characterise the soils for the 2009 field experiment site 1 at Pinjarra, a representative 2 kg sample was taken from seven depths, 0–10 cm, 10–20 cm, 20–30 cm, 30–40 cm, 40–50 cm, 50–60 cm and 60–70 cm. The 0–10 cm soil samples were collected from random locations across the experiment site using a 20 mm hollow metal tube and the 10–70 cm samples were collected using a mechanic auger (Plate 3.2 and Plate 3.3).

To characterise the soils for the 2009 field experiment site 2 at Serpentine, a representative 2 kg sample was taken at three depths: 0–10 cm, 10–20 cm and 20–30 cm. The soil samples were collected using two methods, with 0–10 cm sample collected from random locations across the experiment site using a 20 mm hollow metal tube and the 10–30 cm samples collected by digging a single 30 cm² hole at a single location within each replication. The soil was sieved through a 2 mm screen to remove stones and plant debris, placed in labelled containers and then dried at 50°C for 12 hours before analysis.

Post-experiment samples were collected in early January 2012, with all plots sampled at a depth of 0–10 cm. Samples were taken at both field experiment sites by collecting 20 soil cores from each plot. A single core was collected at 10–20 cm and 20–30 cm depth by digging a single 30 cm² hole and removing the surface layers.

Plate 3.2 Soil in field experiment site 1.

Plate 3.3 Soil in field experiment site 2.

3.3.2 Glasshouse experiments sample collection

Root material was removed and the soil placed into aluminium trays before 0–10 cm of the soil was collected in 2 kg clear polyethylene bags. The soil samples were then analysed as per the experimental design and any of the residual soil sample material was placed into storage. Water samples from the two glasshouse experiments were collected in labelled 100 mL white polyethylene bottles with a screw lid. The samples were then refrigerated at 4°C and/or transported to CSBP Limited laboratory for Inductively Coupled Plasma (ICP) analysis.

Plant tissue samples from the glasshouse experiments were harvested at ground level and placed into paper bags. Wet weights were recorded and then the samples were dried with the dry matter weights were recorded. The tissue samples were then analysed as per the experimental design and then any residual material was placed into storage.

3.3.3 Field experiments sample collection

Plant tissue samples were collected in labelled paper bags. Two types of paper bags were used for collecting the tissue samples: small bags (approximately 15 cm in width and 30 cm in height) for collecting samples for nutrient analysis, and larger bags (approximately 30 cm in width and 50 cm in height) for collecting quadrat cuts for measurement of dry matter yield.

3.3.4 Long-term sample storage

All experimental samples are stored in a manner that reduces the probability of contamination between samples or from external sources, for at least five years after this thesis is published. Soil samples are stored in sealed plastic bags and then placed in into a large plastic tub and covered with plastic sheeting. Plant tissue samples are stored in paper bags, then placed in cardboard boxes and then placed on a standard size pallet and covered in plastic. After water samples had been analysed, the residual water was retained in bottles and frozen at -20˚C in a chest freezer for long-term storage. All physical experimental material is stored at 1289 Mooliabeenee Road, Gingin, Western Australia, with soil and tissue sample stored in a large agricultural shed and the water samples in two chest freezers at a different location at the same address.

3.4 Soil analysis methods

All soil analysis was conducted at CSBP Limited laboratory according to standard analysis procedures outlined by (Loss 2012). The methods and references in this section are publicly available from this laboratory and permission to be published in this thesis has been authorised by the author Dr Stephen Loss (see Appendix 9.3).

Unless specified otherwise, all soils were dried at 40°C for 24 hours or until dry, then crushed and sieved to less than 2 mm. Most of the following methods are based on those described by (Rayment and Lyons 2011). These analytical methods are outlined in: P soil analysis Table 3.4, other soil nutrient analyses Table 3.5, soil physical and chemical analysis Table 3.6, and plant, water and fertiliser analysis methods (see Table 3.7).

3.4.1 International and Australia methods for soil, plant and water analysis

There is no single standard for the analysis of P in soil and the method varies depending on location (Rayment and Lyons 2011). The two currently used methods used in Australia are (Olsen *et al.* 1954; Colwell 1965; ISO 1994). For example, the United States of America prefers the Olsen Method as outlined by Hughes *et al.* (2000) for the analysis of P. Even within Australia the analysis of P varies, with the Eastern Australia states preferring the Olsen method while Colwell is the current standard method in Western Australia (Brennan and Bolland 2007). Analysis of water, plant and material for nutrient content is conducted using inductively coupled plasma (ICP) spectrometry (ISO 1987; Zarcinas *et al.* 1987).

3.4.2 Limitations and analytical methods for soil, plant and water analysis

In this thesis, the samples collected for analysis are only as accurate as the sampling techniques used. The samples collected for this research have been collected to provide a representative sample for a site and is meant to reflect the range of samples from a location since it was not possible to analyse every treatment in the experiment. All analytical methods have some inherent variability in the measurements that they produce because of small variations in sample preparation and instrumentation.

The accuracy of any analysis can vary depending on the type of analysis and as such methodologies have been developed to ensure that any error is minimised and ensure that results are consistence. The reporting limits for the following tests in Australia are: Colwell P (+/- 2), Total P (+/- 1), pH ($CaCl_2$) (+/- 0.2), and EC (+/- 0.01). As analysis is conducted in batches, a number of control samples are included in the batch in random locations that have known results, and these are then checked to ensure that the methods and instrumentation are operating correctly and the results from each sample are accurate.

Table 3.4 Soil analysis methods for phosphorus*.

Analysis	Method	References
Colwell phosphorus and potassium (mg/kg)	"Using a soil to solution ratio of 1:100, soils are extracted with 0.5 M sodium bicarbonate solution adjusted to pH 8.5 for 16 hours. The acidified extract is treated with ammonium molybdate/antimony trichloride reagent and the phosphorus is measured colorimetrically at 880 nm using a discrete analyser. The potassium in the extract is determined using a flame atomic absorption spectrophotometer at 766.5 nm."	(Colwell 1965; Rayment and Lyons 2011)
Olsen (mg/kg)	"Soil are extracted at a ratio of 1:20 with $NaHCO_3$ (pH 8.5) for 30 minutes. The orthophosphate ion reacts with ammonium molybdate and antimonyl tartrate, under acidic conditions to form a phosphomolybdic acid complex. This complex is reduced with ascorbic acid to form a blue complex which adsorbs light at 880 nm and can be detected on a discrete analyser."	(Olsen *et al.* 1954; Rayment and Lyons 2011)
Total phosphorus	"Soils are digested in sulphuric acid in the presence of a BDH Kjeldahl catalyst tablet in a microwave. The total P concentration measured colourimetrically at 880 nm after incubation with the colouring reagent ammonium molybdate/potassium antimonyl tartrate in an acid medium."	(Allen and Jeffery 1990b; Rayment and Lyons 2011)
Acid extractable	"Acid extractable P can be used to measure the labile P component in the pool. The test favour's extraction of Ca-bound P, many forms of which are not available to plants and, as such, the test can overestimate P availability. Soils are extracted for 16 hours with 0.005 M sulphuric acid and the P in the cleared extract is determined colourimetrically on a discrete analyser."	(Rayment and Helyar 1980; Rayment and Lyons 2011)
Phosphorus buffering index (PBI)	"Phosphorus Buffering Index is measured by the amount of P sorbed by the soil when the solution concentration of P is increased by 100 (mg/mL). After extraction with a calcium chloride (+) sodium dihydrogen phosphate solution, this method determines the phosphorus buffering index of soils colorimetrically with ammonium molybdate/ammonium metavanadate reagent using a discrete analyser."	(Allen and Jeffery 1990b; Rayment and Lyons 2011)
Phosphorus retention index (PRI)	"Phosphorus retention index is defined as the ratio of the adsorbed phosphorus to the equilibrium concentration. The amount of phosphorus adsorbed/desorbed by each gram of the soil pads is the difference between the initial concentration of phosphorus (Po) and the equilibrium concentration (Peq). Phosphorus in soils is extracted in a 0.02 M potassium chloride equilibrating solution in a ratio of 1:20 for 16 hours, and the concentration of P in the resulting solution (Peq) is determined colorimetrically on a discrete analyser."	(Allen and Jeffery 1990b)

*(Loss 2011)

Table 3.5 Other soil nutrient analyses methods.

Analysis	Method	References
Nitrate and ammonium (mg/kg)	“Soil nitrate nitrogen and ammonium nitrogen are extracted with a 2 M potassium chloride solution for 1 hour at 25°C. After dilution the resulting soil solution is measured on a Lachat Flow Injection Analyser. Ammonium is measured colorimetrically at 630 nm using the indo-phenol blue reaction. Nitrate is reduced to nitrite through a copperised-cadmium column and the nitrite is also measured colorimetrically at 520 nm.”	(Searle 1984; Rayment and Lyons 2011)
Sulphur (mg/kg)	“Plant available sulphur in soils is determined by extraction with a 0.25M potassium chloride solution for 3 hours at 40°C. The sulphur content of extracts are analysed by Inductively Coupled Plasma Spectrometry. This method is known as the KCl-40 or Blair/Lefroy Extractable Sulphur method.”	(Blair *et al.* 1991; Rayment and Lyons 2011)
Organic carbon (%)	“In the (Walkley and Black 1934) method concentrated sulphuric acid is added to soil wetted with dichromate solution. The chromic ions produced are proportional to oxidised organic carbon and are measured colorimetrically at 600 nm on a plate reader.”	(Rayment and Lyons 2011)
Total K (Kjeldahl)	“Total K samples are digested with sulphuric acid and a Kjeldahl copper catalyst tablet in a microwave. Diluted samples are read for K using a flame atomic absorption spectrophotometer at 766.5 nm.”	(Allen and Jeffery 1990a)
Skene K (HCl)	“This test is used to determine the available K fraction in the soil. Skene K values are typically lower than Colwell K values when the soils being tested are alkaline. Soils are extracted for 1 hour in 0.05 M hydrochloric acid and the resulting extract is read for K using a flame atomic absorption spectrophotometer at 766.5 nm.”	(Haysom 1971; Rayment and Lyons 2011)
Total nitrogen	“Total nitrogen is determined by Dumas high temperature combustion (LECO analyser), where soil samples are loaded into a combustion tube at 950°C and flushed with oxygen. All gases generated are collected and measured on an infrared detector for carbon and a thermal conductivity cell for nitrogen.”	(Rayment and Lyons 2011)

Table 3.6 Soil physical and chemical analysis methods.

Analysis	Method	References
Soil pH and electrical conductivity (ds/cm)	“Using a soil to solution ratio of 1:5, soils are extracted in deionised water for 1 hour. The water pH and electrical conductivity of the extract are measured using a combination pH and conductivity electrode. After the water pH and EC have been measured, calcium chloride solution is added to the soil solution to the equivalent of 0.1 M and after thorough mixing for 10 minutes the calcium chloride pH is also measured. All measurements are recorded while the solution is stirred.”	(Rayment and Lyons 2011)
Texture	“Texture is assessed by wetting the soil and feeling the wet soil between the forefinger and thumb. Six texture categories are used: sand (1.0), loamy sand (1.5), loam (2.0), clay loam (2.5), Clay (3.0) and heavy clay (3.5).”	
Colour	“Soils are classified into the following colours: white, grey, yellow, brown, orange, red, pink and black. More than one colour may be included (e.g. brown yellow) and light and dark may also be assigned.”	(Munsell 2000)
Gravel content	“The gravel content is estimated visually and by running the fingers through the soil. Approximate figures are reported, e.g. 10–15 (%).”	
Physical observations	“Unprepared soil samples are laid on a cardboard tray and soil texture, colour and gravel content are estimated by a quick physical observation. These procedures were devised to give an indication whether the soil type changed between samples, not as an accurate measurement of the soil characteristics. Our classification systems do not correspond to any other systems, e.g. Northcote classification”	(Northcote 1979)
Particle size	“Prepared soil samples are treated with hydrogen peroxide to remove the organic matter, and then shaken with a 1:1 Calgon-Sodium Hydroxide mixture to disperse the soil particles. Using a table of particle sedimentation times, 25 mL aliquots of the solution are removed at the set times and the remaining sample is sieved. The aliquots are evaporated in an oven and weighed to determine the coarse and fine sand, silt and clay contents”	(Indorante *et al.* 1990)
Moisture, ash and organic matter (%)	“Fresh soil samples are weighed heated in a furnace to 100°C overnight and weighed a second time to determine percentage moisture. Soils are then heated in a furnace at extreme temperatures to determine loss on ignition (400°C for 4 hours) and percentage ash (600°C for 2 hours) values. Loss on ignition and percentage ash measurements are used to estimate of organic matter content of the soil.”	(Rayment and Lyons 2011)
Exchange acidity (meq/100 g)	“Soils are extracted with 1 M KCl in a 1:5 ratio for 1 hour, and the exchangeable acidity Al^3+ and H+ are measured by titration with NaOH and hydrochloric acid. Exchangeable Al^3+ and H+ are held on exchange sites is largely dependent on the pH of the soil. The method for Al can be used to replace $CaCl_2$ extractable method and the exchange acidity value is particularly useful for high pH soils.”	(Rayment and Lyons 2011)

3.5 Plant and water analysis

Unless specified otherwise, plants samples were dried at 40°C for 24 hours or until dry, and then ground and sieved through 2 mm. Water samples were analysed for pH, electrical conductivity, nitrate and ammonium according to the methods described for soils and multi-element analysis are determined by inductively coupled plasma. Total dissolved solids can be calculated from the electrical conductivity results. These analytical methods are outlined in Table 3.7.

Table 3.7 Plant, water and fertiliser analysis methods.

Analysis	Method	References
Multi-elements (ICP) (mg/kg) (plant)	"After complete digestion of the plant material with a combination of nitric acid and hydrogen peroxide at high temperatures, digest solutions are diluted with deionised water to dissolve all precipitates. The resulting solutions are subsequently analysed on the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) for determination of the elements, boron, copper, zinc, manganese, iron, calcium, magnesium, sodium, potassium, phosphorus and sulphur. They can also be read for molybdenum, cobalt and selenium."	(McQuaker *et al.* 1979)
Nitrates and chlorides (mg/kg) (plant)	"Plant nitrate and chloride are extracted by stirring plant material in deionised water for 30 minutes. The extracted nitrate is reduced to nitrite in a copperised cadmium column and the nitrite determined colorimetrically on the Lachat Flow Injection Analyser at 520 nm. For chloride the reaction is based on the liberation of thiocyanate ions from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms ferric thiocyanate which is read colorimetrically at 480 nm in a flow injection analyser."	(Instruments 2012)
Water analysis (mg/L)	"Water samples were analysed for pH, electrical conductivity, nitrate and ammonium according to the methods described for soils and multi-element analysis are determined by inductively coupled plasma. Total dissolved solids can be calculated from the electrical conductivity results."	
Phosphate fertilisers	"This method determines the water-soluble phosphorus content in calcium phosphate fertilisers containing > 10% Phosphorus and Superphosphate in all stages of manufacture. The differences in phosphate solubility of SSP and LWSSP, such as P % (total), P % (monobasic calcium phosphate) and P % (dibasic calcium phosphate) were measured by established method and the P % (dibasic calcium phosphate) was determined by subtracting the measured P % (monobasic calcium phosphate) and P % (tribasic calcium phosphate) from the P % (total)."	(McQuaker *et al.* 1979)

3.6 Fertiliser Analysis

The methods outlined in this section were derived from three CSBP Limited standard laboratory procedures (Morris 2015c, 2015b, 2015a). The chemistry of MCP, DCP and TCP is outlined in Table 3.8, the analysis of SSP and LWSSP is outlined in Table 3.9 and the basal fertiliser applied to glasshouse experiments is outlined in Table 3.11 and Table 3.12. The predicted solubility of each fertiliser treatment applied to glasshouse experiment 1 is outlined in Table 3.10 with SSP and LWSSP calculated from the percentages of MCP, DCP and TCP. All of the fertiliser analysis in this research was conducted at CSBP Limited Kwinana fertiliser laboratory.

Table 3.8 Chemical forms of phosphate in single superphosphate fertiliser.

Type	Solubility	Chemical analysis
Monobasic calcium phosphate	Water-soluble	$Ca(H_2PO_4)_2\ H_2O$
Dibasic calcium phosphate	Citrate-soluble	$CaHPO_4\ 2H_2O$
Tribasic calcium phosphate	Citrate-insoluble	$Ca_3\ (PO_4)_2$

Table 3.9 Phosphorus concentrations (%W/W) in fertiliser use.

Type	SSP	LWSSP
Total P	9.1	8.3
Monobasic calcium phosphate^A	7.8 (86)	2.9 (35)
Dibasic calcium phosphate^A	0.8 (9)	3.7 (45)
Tribasic calcium phosphate^A	0.5 (5)	1.7 (20)

Values in parentheses are a percentage of total phosphorus.
Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP).
^{A} Measured by standard (AOAC 1975).

Table 3.10 Total predicted solubility of each treatment applied to glasshouse experiment 1.

Fertiliser	MCP (%)	DCP (%)	TCP (%)	Total calculated solubility (%)
MCP	100	0	0	99.9
DCP	0	100	0	36.2
TCP	0	0	100	0.01
SSP	86	9	5	89.2
LWSSP	35	45	20	51.3

Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), single superphosphate (SSP) and low water-soluble superphosphate (LWSSP). Calculations used to determine total calculated solubility are based on 40 L of water outlined in Appendix 9.3.2.3 (Kotz *et al.* 2003).

Table 3.11 Glasshouse experiment 1 (hydroponics) basal nutrient solution (total applied to each system per run), Hydroponics basal nutrient mixture was designed and supplied by HyGen Limited (Perth, Western Australia).

Boron (mg)	Calcium (mg)	Copper (mg)	Iron (mg)	Magnesium (mg)	Manganese (mg)	Phosphorus (mg)	Potassium (mg)	Sodium (mg)	Sulphur (mg)	Zinc (mg)
13.14	4797.28	5.25	80	1461	35	0.11	7007	131	1753	6

Table 3.12 Glasshouse experiment 2 (pot) basal nutrient solutions (applied per kg of soil).

Boron (mg)	Calcium (mg)	Chorine (mg)	Cobalt (mg)	Copper (mg)	Magnesium (mg)	Manganese (mg)	Mo (mg)	Nitrogen (mg)	Phosphorus (mg)	Potassium (mg)	Sulphur (mg)	Zinc (mg)
0.1	41	98	0.1	0.5	4	3	0.08	33	< 0.05	89	34	2

* 0.23 mL per pot of urea ammonium nitrate-nitrogen and sulphur were also applied.

3.7 Experimental approach for experiments

Demineralised water was used in the glasshouse experiments. Analysis of the demineralised water showed that nutrients concentrations (Boron, calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, sulphur and zinc) were less than 0.05 (mg/L). The demineralised water was sourced from CSBP Limited ammonium nitrate manufacturing plant number one Kwinana, Western Australia and placed into 20-litre plastic drums for transport to experimental areas as required.

3.7.1 Design for glasshouse experiment 1

3.7.1.1 Glasshouse experiment 1 (hydroponics)

For this hydroponics experiment, a factorial experimental design was used with the 2 plant-type treatments (Clover, Ryegrass), 6 fertiliser treatments (Nil, SSP, LWSSP, MCP, DCP, and TCP) and with 3 replicates (see Table 3.13). The treatment placement within/between replicates was also spatially adjusted to minimise the treatment covariances using trial program DiGGer. The final treatment design is shown in Appendix 9.3.2.1.

Table 3.13 Hydroponics experimental design.

Trt	Plant species	Fertiliser
1	Clover	Nil-P
2	Ryegrass	Nil-P
3	Clover	Single superphosphate
4	Ryegrass	Single superphosphate
5	Clover	Low water-soluble superphosphate
6	Ryegrass	Low water-soluble superphosphate
7	Clover	Monobasic calcium phosphate
8	Ryegrass	Monobasic calcium phosphate
9	Clover	Dibasic calcium phosphate
10	Ryegrass	Dibasic calcium phosphate
11	Clover	Tribasic calcium phosphate
12	Ryegrass	Tribasic calcium phosphate

3.7.1.2 Leaching column

For the leaching column experiment, a factorial experimental design was used with 6 fertiliser treatments (Nil, SSP, LWSSP, MCP, DCP, and TCP) and with 3 replicates (see Table 3.14). The treatment placement within/between replicates was also spatially adjusted to minimise the treatment covariances using trial program DiGGer. The final treatment design is shown in Appendix 9.3.2.2.

Table 3.14 Leaching column experimental design.

Trt	Fertiliser
1	Nil-P
4	Monobasic calcium phosphate
5	Dibasic calcium phosphate
6	Tribasic calcium phosphate
7	Single superphosphate
8	Low water-soluble superphosphate

3.7.2 Design for glasshouse experiment 2

For glasshouse experiment-2, a factorial experimental design was used with the 2 plant-type treatments (Clover, Ryegrass), 3 soil types (heavy, medium, and light), 3 fertiliser treatments (Nil, SSP, LWSSP) and with 3 replicates (see Section 3.15). The treatment placement within/between replicates was also spatially adjusted to minimise the treatment covariances using trial program DiGGer. The final treatment design is shown in Appendix 9.3.3.

Table 3.15 Pot experimental design.

Trt	Plant spices	Soil	Fertiliser
1	Clover	Heavy	Low water-soluble superphosphate
2	Clover	Heavy	Nil-P
3	Clover	Heavy	Single superphosphate
4	Nil	Heavy	Low water-soluble superphosphate
5	Nil	Heavy	Nil-P
6	Nil	Heavy	Single superphosphate
7	Ryegrass	Heavy	Low water-soluble superphosphate
8	Ryegrass	Heavy	Nil-P
9	Ryegrass	Heavy	Single superphosphate
10	Clover	Light	Low water-soluble superphosphate
11	Clover	Light	Nil-P
12	Clover	Light	Single superphosphate
13	Nil	Light	Low water-soluble superphosphate
14	Nil	Light	Nil-P
15	Nil	Light	Single superphosphate
16	Ryegrass	Light	Low water-soluble superphosphate
17	Ryegrass	Light	Nil-P
18	Ryegrass	Light	Single superphosphate
19	Clover	Medium	Low water-soluble superphosphate
20	Clover	Medium	Nil-P
21	Clover	Medium	Single superphosphate
22	Nil	Medium	Low water-soluble superphosphate
23	Nil	Medium	Nil-P
24	Nil	Medium	Single superphosphate
25	Ryegrass	Medium	Low water-soluble superphosphate
26	Ryegrass	Medium	Nil-P
27	Ryegrass	Medium	Single superphosphate

3.7.3 Design for field experiments

For the field experiments, a randomised complete block (RCB) experimental design was used with the 3 fertiliser treatments (Nil, SSP, LWSSP), 5 application rates (0, 5, 10, 15, 25 kg/ha) and with 3 replicates (see Table 3.16). The final treatment design for each field experiment is outlined in Appendix 9.3.4.

Table 3.16 Field experimental design.

Trt	Fertiliser	Amount of applied P (kg/ha)
1	Nil-P	0
2	Low water-soluble superphosphate	5
3	Single superphosphate	5
4	Low water-soluble superphosphate	10
5	Single superphosphate	10
6	Low water-soluble superphosphate	15
7	Single superphosphate	15
8	Low water-soluble superphosphate	25
9	Single superphosphate	25

Basal solids fertiliser applications included muriate of potash, granular sulphate of ammonia, lime and urea. The basal liquid fertiliser applications included urea ammonia nitrate and urea ammonia nitrate sulphur. The application rates and dates of applications of all fertilisers are listed in the appendix (see Section 9.3.4).

3.7.3.1 Site management

Broad-leaf weeds, predominantly capeweed were controlled with Tiger X, a selective herbicide with MCPA (present as the iso-octyl ester) as the active constituent. Tiger X was periodically applied throughout the growing season at rates up to 1 L/ha (rate as per requirement by Blacklow (2008b) to ensure the pasture composition was dominated by clover and ryegrass. Insects, predominantly red-legged earth mites, were controlled with Lemat, an insecticide with Omethoate as the active constituent. This insecticide was periodically applied throughout the growing season at rates up to 300 mL/ha (rate as per requirement by Blacklow (2008a) to reduce the chance of insect damage. Electric fencing was erected around half of each field experiment to exclude cattle and allow pasture measurements. The fencing was separated into two sections (front and rear) to allow one section to be excluded from grazing and then measured at the optimum level of dry matter growth (2–2.5 t/ha), and then the fence was shifted to the other section which had been grazed. This design enabled pasture growth to be measured continuously over the season. Areas of cattle dung were avoided for all measurements so as not to bias the results.

3.8 Data collection

3.8.1 Dry matter yield

Dry matter yield was determined by three different methods:

1) Removing the whole sample.
2) Rising plate meter calibrated using quadrat cuts.
3) Quadrat cuts from a representative area of the experiment plot.

Removing the whole sample was the most accurate method for determining dry matter yield for the glasshouse experiments. The plant tissue was cut at 1 cm above the surface of the pot and oven dried. The dry matter yield was determined using the following (see Equation 3.1).

Equation 3.1

$$\text{DM (t/ha)} = \frac{tissue\ dry\ weight\ (g)}{surface\ area\ of\ pot\ (cm2)} \text{ x } 100$$

Measuring dry matter yield with a rising plate meter is a well-established method as defined by McQuaker *et al.* (1979) that allows a large number of plots to be measured in a non-destructive way. A rising plate meter is an instrument with a square plate that is allowed to move up and down placed on the surface of the pasture and has a counter that measures the height of the pasture. As some readings are taken (30 per plot), the average height of the plants can be determined, and the process is repeated for all plots within the field experiments. Once an average range of plate meter readings is known, the plate meter is then used to find a quadrat area (1 m^2) of pasture within the average range. A dry matter cut is then taken from within this quadrant area (1 m^2) to calibrate that height of the plate meter and the process is repeated at least 8 times to cover the range of the average plate meter readings. The quadrat cuts were then dried and weighed, with the dry matter weights multiplied by 40 and plotted against the rising plate meter that was taken from this quadrant and a linear line of best fit fitted. This line is used to determine the dry matter yield for all reading taken from the experiment using (see Equation 3.2).

Equation 3.2

$$\text{DM (t/ha)} = \frac{Yield\ x\ average\_plate\_reading + X}{1000}$$

Quadrat cuts were also used to determine the dry matter yield for each plot of the field experiments by taking a single cut from a representative area of the plant growth within that plot. The cuts were then dried and dry matter yield was determined using (see

Equation 3.3). This method is less accurate and was only used for plants that had moved towards the reproductive phase of their life cycle, and the rising plate meter could not accurately determine the plant height.

Equation 3.3

$$\text{DM (t/ha)} = \frac{quadratcut\_dried\_weight\ x\ 40}{1000}$$

3.8.2 Tissue analysis and plant uptake

Tissue analysis was conducted using two methods:

1) Removing the whole sample.
2) Removing a representative sample.

Analysing the whole sample was conducted for the glasshouse experiments after the dry matter yield was determined. Due to the low dry matter weight obtained from the glasshouse experiments, the samples were bulked together according to treatment to ensure there was enough material to analyse.

Plant tissue analysis of the field experiment was conducted using the representative sampling method with ‘grab’ samples taken from 10 random locations within the plots. Grab samples were taken by preferentially selecting a single species (usually clover) to be consistent and removing the top leaves of the plants. If the amount of clover was inadequate for a sample, ryegrass was selected and the species recorded.

For all experiments, plant uptake of P was used to determine the total amount of P removed by the given treatment. This method was adjusted to account for the dilution of a nutrient as the amount of dry matter increased. Plant uptake was determined using (see Equation 3.4).

Equation 3.4

Plant uptake equals (dry matter yield (t/ha) multiplied by tissue P (%)) multiplied by 10.

$$\text{Plant update} = \text{DM\_yield(t/ha)} \times \text{tissue\_P(\%)} \times 10$$

3.8.3 Water samples

Water samples collected from the glasshouse experiments using two methods:

1) Hydroponics samples.
2) Leachate and pot samples.

Hydroponic samples were collected through the pot watering system that transfers tank solution to the perlite pots. The plastic bottle was then placed into one of the six pipes that were placed on the top of the pots until it was filled. This method was used to ensure the sample collected was the same as the solution being pumped over the pots. Leachate samples collected from experiment 2 were collected from clear plastic bags placed below the pots or columns. The volume of the leachate was recorded first and then if a P concentration measurement was required, the bag was then shaken to ensure the nutrients were distributed throughout the sample and then a 100 mL collection bottle was filled.

3.8.4 Visual observations

Visual observations (i.e. often photographs) of all experiments were recorded to support quantitative analyse and when accurate measurements using the outlined dry matter yield methods were not possible. All experiments had photographic records taken for dry matter yield measurements and checked against laboratory analysis to confirm the accuracy of the quantitative analysis.

3.9 Experimental equipment and design specifications

3.9.1 Glasshouse experiment 1

3.9.1.1 Hydroponics

The hydroponics systems were custom designed with support from Perth Aquaponics, Belmont Western Australia. The design contained three identical tanks, comprising six pots per tank and a single P treatment applied to each tank. The cooling tanks where arranged in a U-shaped configuration and placed into three large tubs used as cooling jackets to ensure an even temperature of all three systems. The tubs were then connected by 19 mm poly pipe to allow the water to interchange between each tank (see Figure 3.5). The hydroponic tanks were 340 mm (high), 600 mm (wide) and 450 mm deep (92 litres).

The system design and placement are shown in Plate 3.4 and Plate 3.5. Each hydroponic tank was then placed into a large cooling tank, 360 mm height, 810 mm wide and 540 mm deep (157 L volume). The cooling tanks were filled with tap water 190 mm (approx. 35 litres) to maintain an even temperature across the three hydroponic tanks. The experiment was conducted in a clear glasshouse with refrigerated air conditioning set at 22°C to maintain a constant air temperature.

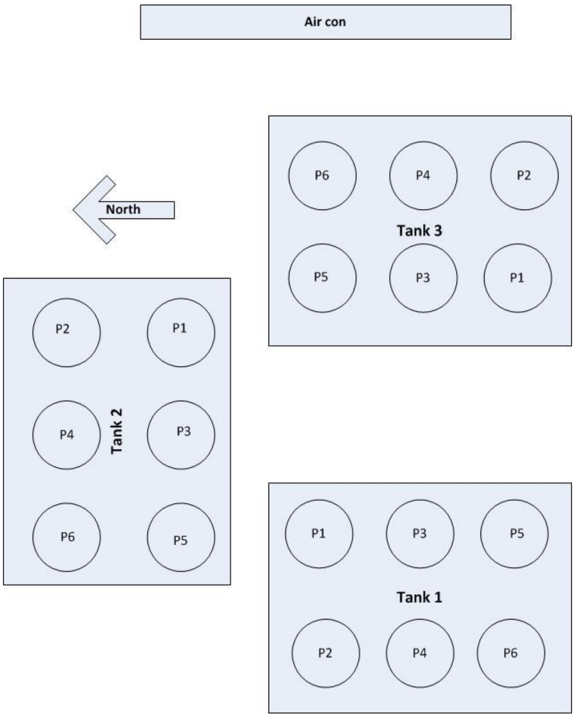


Figure 3.5 Schematic layout of the hydroponic system.

Plate 3.4 Hydroponic tank 1 with 6 pots placed into the lid.

Plate 3.5 Layout of the hydroponic tanks in the glasshouse.

Polyvinyl chloride pots (125 mm diameter, 100 mm deep) were filled with perlite to approximately 1 L of volume.

The internal system contained two elements:

1) An aeration stone and air pump (AQUA PRO, AQUARIUM AIR PUMP S90) was used to continuously pump air from the bottom of the tank to agitate the nutrient solution and ensure an even nutrient distribution for the duration of the experiment.

2) A pumping and distribution system that pumped the used nutrient solution over the pots where it would flow over the roots and return to the tank in a closed system for recycling.

The air pump (AQUA PRO, WATER FEATURE PUMP AP550) was placed at the bottom of the tank and protected within a hydroponic pot to stop any material or plant roots from blocking the pump. The pump was then connected to a ring main to ensure that the pressure was even and the six small diameter pipes were then connected into the ring main pipe. Each of the six pipes was then connected to an individual pot though the cover of the tank for the liquid delivery to the plants. The nutrient solution and treatment fertiliser pumped onto the surface of the perlite. The nutrient pumping and distribution were run for 30 minutes of every hour for 11 hours per day (7 am to 6 pm).

Each tank had 40 L of demineralised water applied at the beginning of each 21 day experimental run and an additional 2 L applied at 14 days to ensure that water levels within the tanks remained above the level of the pump. The addition of 2 L was required as the system's water gradually reduced in volume due to evaporation and transpiration over the 21 days.

Possible experimental errors which were caused by the equipment and environment are:

- Nutrient levels within treatments with high water-soluble P decreased as plant growth increased.
- The amount of daylight for plant growth varied throughout the three-month experiment.
- The physical location of the each tank in relation to light and distance from the air conditioning may have caused a slight variation of growth for the same treatment in each of the three tanks.

These problems were accounted for through the uses of statistical analysis and the randomised experimental design throughout the experiment. Supplementary notes and information related to this experiment (see Appendix 9.3.2).

3.9.1.2 Leaching column experiment

The leaching column experiment was conducted in polyvinyl chloride pots (152 mm diameter, 400 mm deep) packed with perlite for a total volume of 6 L (see Plate 3.6). A fine stainless steel mesh was placed at the bottom of each column to retain any particles, not in solution. The columns were placed on two small benches in four rows with a circular hole cut out of the bottom to allow a collection bag to be placed beneath each column (see Plate 3.7 and Figure 3.6). The columns were pre-leached with demineralised water to the equivalent of 164 mm rainfall. The fertiliser treatments were applied to the surface of the columns. Each rainfall event was simulated by using a small plastic water can apply 1.5 L of demineralised water in a circulating manner to ensure even coverage across the surface of each column. The columns were watered three times per week on Monday, Wednesday and Friday and then allowed to drain for a minimum of 48 hours before the next watering. Water samples in clear plastic bags (approximately width 20 cm and height 30 cm) were collected just before the next watering, and a 100 mL subsample was taken and then refrigerated at 4°C until they were transported to the laboratory for analysis. After each watering, a plastic cover was placed over the surface of all the columns to eliminate contamination from other sources.

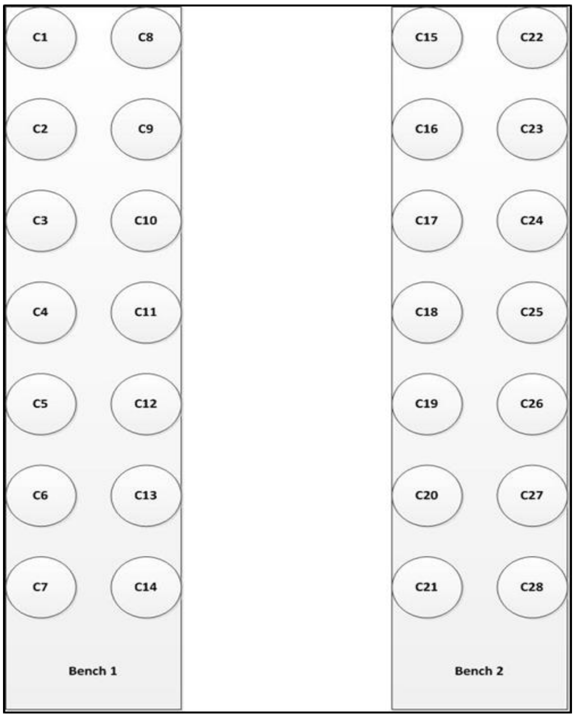


Figure 3.6 Layout of the leaching columns and benches.

Plate 3.6 Leaching column filled with 6 L of perlite prior to the start of the experiment.

Plate 3.7 Leaching columns in position on the bench with the phosphorus fertiliser treatments applied to the surface. Note the clear plastic bag placed below each column for a collection of the leachate.

Appendix 9.3.3 contains all supplementary notes and information related to this experiment.

3.9.2 Glasshouse experiment 2

Polypropylene pots (130 mm diameter, 135 mm deep, 1.25 L in volume) were filled with the required weight of soil to fill the pot to 10 mm below the surface of the pot. The light and medium soils were applied at 2.0 kg/pot while the heavy soil was applied at 1.4 kg/pot to ensure the volume of all three soil types was kept constant.

The pots had coffee filters applied to their base, held in place with rubber bands to ensure that no soil would be lost and only nutrients in solution would be leached. A total of 27 treatments were replicated 3 times in a randomised block design (see Figure 3.7). All pots were seeded with 20 seeds per pot using a pair of tweezers to drop a single seed into a hole no more than 10 mm below the soil surface. Ten days after the seeding had germinated the plants were thinned to 10 plants per pot (see Plate 3.9).

Plastic bags were placed below each pot for collecting leachate and were replaced, as required if a leak or algal growth occurred (see Plate 3.9). Using a garden pressure sprayer, demineralised water was sprayed over the soil to block the holes. All supplementary notes and information related to this experiment are outlined in Appendix 9.3.3.

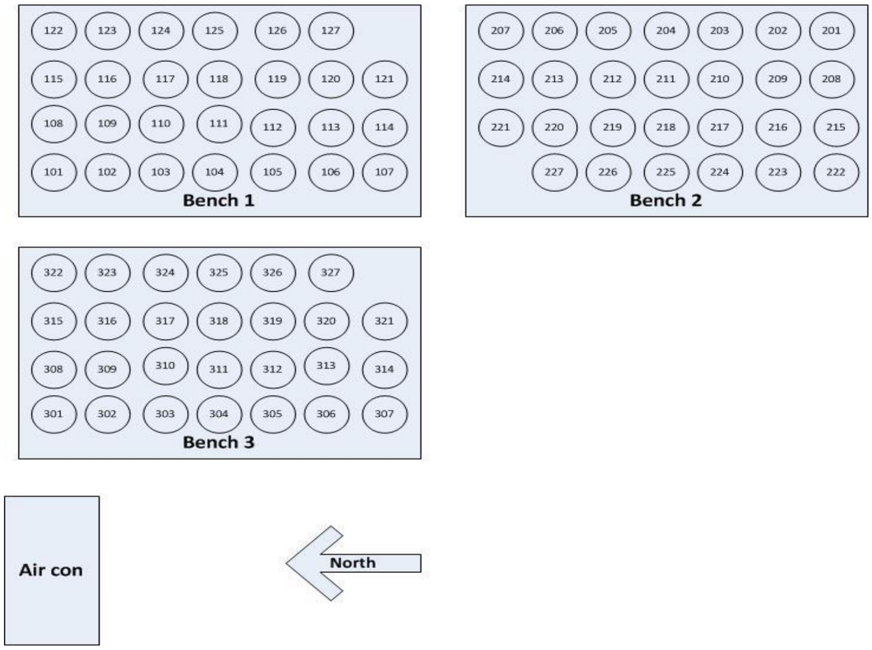


Figure 3.7 Layout of the pot experiment.

Plate 3.8 Layout of bench 1 of the pot experiment.

Plate 3.9 Leachate collection bags under the pots on the bench 1 of the pot experiment.

3.9.3 Field experiments

The two field experiments were selected based on location, soil type and pasture system. Each field experiment had 27 plots that were pegged at 2.75 m wide and 20 m long to allow application of fertiliser treatments using either the cone top-dresser (Plate 3.10) or spread by hand. Liquid fertilisers, herbicides and pesticides were applied using a four-wheel quad bike fitted with a boom spray (Plate 3.11) and were applied across the width of the experiment. Each field experiment was 74.25 m wide and 20 m long for a total of 1485 m^2. The plots were divided into 10 m long sections using electric fencing to exclude cattle. The electric fencing was erected by placing six copper logs at each of the corners of experiment and two at 10 m to divide the experiment into two sections. Star pickets with plastic insulators were then placed between the copper logs front to allow the electric fencing tap to be connected up to the required section. Nine treatments were replicated 3 times and the randomised block design outlined in Figure 3.8. Field experiments were conducted with a number of standard pieces of equipment. All supplementary notes and information related to this experiment are outlined in (see Appendix 9.3.4).

Figure 3.8 Layout of the field experiments.

Plate 3.10 Cone top-dresser used to apply an even application of granular fertilisers and lime to the field experiment sites.

Plate 3.11 Four-wheel quad bike used for applying of liquid fertilisers, herbicides and pesticides to the field experiment sites.

3.10 Statistical analysis, calculations and data storage

The data was recorded on worksheets or direct into a data logger for loading into Microsoft Excel. After validating the data against the original worksheets, the data was loaded into Genstat (version 16) and summarised across replicates to identify outliers. The Genstat definition of an outlier is three standard deviations away from the mean (Nelder 2014). This definition was used when no biological reason could explain the variation in the data. The data for each experiment was then summarised separately before statistical analyses were applied on an individual or combined datasets.

3.10.1 Experimental designs

Experiments in glasshouses and/or field-based experiments may be compromised due to soil trends across the field experiment or amount of light on a bench in the glasshouse. Experimental trial designs that minimise the between plot co-variances or incorporation of autoregressive spatial trends can be undertaken using software such as Cyc-design (https://www.vsni.co.uk/software/cycdesign/) and DiGGer (http://www.austatgen.org/files/software/downloads/). This software was used in this thesis to ensure best possible precision between treatments. These experimental designs are often superior to standard randomised complete block or factorial trials since the treatments and/or plot/pots are stratified across the replicates.

3.10.2 Statistical analysis

The Genstat 'Analysis of Variance (ANOVA)' was used for statistical analyses from a balanced set of data without missing a treatment or spatial effects. The Genstat 'Unbalanced Analyses of Variance (UAOVA)' was used when a treatment combination was missing and again not significant spatial trends. The UAOVA is based on regression analyses methodology to generate the predictions, and the variance estimates for testing significant treatment effects (Nelder 2014).

In situations where there is a spatial trend in the field or glasshouse, a Restricted Maximum Likelihood regression (REML) model within Genstat was used to generate the predictions and variance estimates. The REML function in Genstat allows for fitting a random autoregressive trend to the rows and/or columns in an experiment. If the correlation from the auto-regressive trend was significant, then the REML output was used to generate the predictions. These REML models with fixed effects for treatments and random rows x column effects also can be used in situations of unbalanced data. Please note that the REML fixed effect for treatment models (without random row and/or columns) will give the same predictions as ANOVA for balanced data and UAOVA for unbalanced data (Gilmour *et al.* 1995).

3.10.3 Calculations

From the statistical analyses using Genstat, means, standard errors and least significant difference estimates were generated, and the results (i.e. Residuals plots checked for outliers) before the summaries were used in presentations, figures and tables. Appendix 3.4.5 contains an example of the statistical analyses.

3.10.4 Data storage

All procedures of data storage follow the Australian code for the responsible conduct of research (Heaslop and Salisbury 2007).

3.10.4.1 Digital data

All electronic data collected is stored in accordance with Curtin University guidelines as defined by Heaslop and Salisbury (2007) and data produced from this research is stored on a computer protected by passwords and stored in a safe and secure location. It will also be held in another geographical location for a period of five years after this thesis is published. The data has been duplicated onto a number of separate devices to ensure that a single device failure will not result in the loss of the research results.

3.10.4.2 Physical

Physical copies of data collected and produced are stored in a locked filing cabinet located at my home personal residence.

CHAPTER 4 HYDROPONIC EXPERIMENT

4.1 Introduction

Phosphorus (P) is an indispensable element for plant life with increasing concern about the future of the global supply of P stimulating increased research into soil P (Kruse *et al.* 2015). The use and role of P in agriculture are well documented, with several recent reviews including (Khasawneh *et al.* 1980; Foth and Ellis 1988). Phosphorus is an essential nutrient (after N and K) for plant growth, and it is limiting agricultural production in the south-west of Western Australia because the agricultural soils are inherently low in P (Moore 2004). Consequently, P fertilisers are required to maximise pasture production.

Plants need the majority of P during the early growth stages, and it must be in a water-soluble form for plant roots to access (Price 2006). The water-soluble form of P in solution is taken up by the plant (Richardson *et al.* 2009b). Increasing the efficiency of P fertiliser applied for pasture production and reducing the loss from leaching is very important to farmers faced with increasing costs of pasture production (Cornish 2009). Phosphorus use efficiency describes the amount of P applied to a pasture system relative to the amount recovered by the plant (Johnston and Syers 2009). Single superphosphate, which is designed to have a high percentage of water-soluble phosphorus that is plant available as defined by Prochnow *et al.* (2008), is currently the main P fertiliser used for pasture production. The problem with water-soluble P is that it can be readily leached when applied to soils that have a low ability to retain P (Weaver *et al.* 1988).

The loss of applied P is a well-understood problem and a number of strategies have been developed to slow the release of P from SSP including: coating the surface of SSP with bauxite residue Summers *et al.* (1999a), coating polyethylene film to the surface of fertiliser Pauly *et al.* (2002), and changing the soil properties to increase P retention (Summers *et al.* 1993b; Pathan *et al.* 2002). However, none has been widely adopted because of cost, practicality or public concern. Therefore, a method is needed to reduce the solubility of P fertiliser to match the plant's requirements, while overcoming the problems mentioned earlier. To reduce the solubility of SSP fertiliser, Edmeades (2000) proposed that changing the chemical analysis would achieve similar yield improvements relative to existing SSP. A change in solubility would enable existing manufacturing equipment to be used without alternative approaches such as using slow-release coatings (Nyborg *et al.* 1996).

Fertilisers derived from rock phosphate, such as SSP are comprised of three forms of phosphate that differ in solubility: MCP is water-soluble, DCP is citrate-soluble, and TCP which is citrate-insoluble (see Table 4.1). Monobasic calcium phosphate is the most soluble and the solubility reduces as the ratio of calcium to phosphate atoms increase. Single superphosphate fertiliser is manufactured by crushing of rock phosphate and then applying sulphuric acid; this process can be modified through the application of lime-sand and altering processing methods to manipulate the ration of MCP, DCP and TCP.

Table 4.1 Chemical form, solubility and chemical structure of phosphate fertiliser derived from rock phosphate.

The three forms of phosphate present in fertilisers derived from rock phosphate with their solubilities and their chemical analysis. Monobasic calcium phosphate being the most soluble with the solubility reducing the ratio of calcium to phosphorus atoms increases.

Chemical forms	Solubility	Chemical analysis
Monobasic calcium phosphate	Water-soluble	$Ca\ (H_2PO_4)_2\ H_2O$
Dibasic calcium phosphate	Citrate-soluble	$CaHPO_4\ 2H_2O$
Tribasic calcium phosphate	Citrate-insoluble	$Ca_3(PO_4)_2$

Converting rock phosphate into differing ratios (MCP, DCP, TCP) using acid for plant production is outlined by (Mclean and Wheeler 1964). The overall chemistry of converting rock phosphate to SSP is described as rock phosphate $Ca^3(PO_4)_4$ + H_2SO_4 + H_2O to single superphosphate $Ca(H_2PO_4)_2{\cdot}H_2O$ + Ca_2SO_4 (Agriculture 1964). A more sustainable approach for a pasture production system is to customise the P fertiliser through manipulating the forms of MCP, DCP and TCP in SSP fertiliser to match conditions for plant uptake, thereby decreasing leaching (Summers and Weaver 2008).

It is hypothesised that the P in the fertiliser applied as low water soluble super phosphate (LWSSP) will be less soluble than SSP and hence leach at a lower rate due to a function of its phosphate chemistry. The assumption is once the P is in solution regardless of its phosphate form, that it will be equally available for uptake by plants roots under hydroponic non-soil conditions. Therefore, it is expected that the P fertilisers will dissolve affecting plant dry matter yield and P uptake. The aim of this experiment is to compare P solubility and leaching of LWSSP and SSP fertilisers and their phosphate forms for pasture production in hydroponic no-soil conditions.

4.2 Methods and materials

4.2.1 Hydroponics glasshouse experiment

The study contains two experiments. The first experiment measures the P use efficiency of SSP and LWSSP, which differ in their ratios of MCP, DCP and TCP, and MCP, DCP and TCP in their pure forms for pasture growth in hydroponic conditions. The second experiment measures the solubility of SSP, LWSSP, MCP, DCP and TCP in leaching columns with simulated rainfall and no plants.

The P forms and predicted solubility based on their chemistry as the ratio of calcium to P increases, the solubility decreases as shown in Table 4.2. The solubility of the two P fertilisers (SSP and LWSSP) is a function of their ratio of each phosphate form.

Table 4.2 Phosphorus fertilisers with their composition percentage and phosphorus analysis.

The phosphorus fertilisers used in these experiments with the amount of phosphorus present within each of them and the percentage of the total phosphorus of each phosphate form (within brackets). Single superphosphate (SSP), low water-soluble superphosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP).

	SSP	LWSSP	MCP	DCP	TCP
Total P	9.1	8.3	26.2	18.1	15.9
Water-soluble P[A]	7.8 (86)	2.9 (35)	26.2 (100)	0 (0)	0 (0)
Citrate-soluble P[A]	0.8 (9)	3.7 (45)	0 (0)	18.1 (100)	0 (0)
Citrate-insoluble P[A]	0.5 (5)	1.7 (20)	0 (0)	0 (0)	15.9 (100)

[A] Measured by standard (AOAC 1975).

The design comprised three replicates of 12 treatments; six fertiliser treatments – SSP, LWSSP, MCP, DCP, TCP and a nil-P on two common pasture species used on the SCP, Dalkeith subterranean clover (*Trifolium subterranean* L.) and Wimmera annual ryegrass (*Lolium rigidum)*. The experiment comprised a total of 108 pots divided into 6 experimental runs of 18 pots per run.

Polyvinyl chloride pots (125 mm diameter, 100 mm deep and a volume 1 litre were packed with perlite and then 25–30 seeds of clover or ryegrass were sown in each pot. The pots were placed in aluminium trays and handed watered with demineralised water and a nutrient solution Table 4.3 for 21 days applied three days per week. The trays were filled with demineralised water to ensure pot dampness and aid in seed germination. At 21 days after sowing, each pot was thinned to 20.

The pots were then placed into black Polyvinyl chloride hydroponic tanks for 21 days (i.e. one experimental run). The pots were randomised in the tank (i.e. one treatment per tank) and three pots of each species per tank (i.e. 6 pots per tank) with three tanks per experimental run.

The concentration of P in the P treatments are listed in Table 4.2. Phosphorus treatments were applied as a single application at the beginning of the experiment at 25 kg/ha of P based on the combined surface area of the six pots. The P fertiliser treatments were weighted into two glass plates and placed at diagonally opposing corners of each tank. The SSP and LWSSP were made in Western Australia at CSBP Limited, Kwinana and the MCP, DCP and TCP were imported from China. The fertiliser was crushed and then sieved with particle sizes ranging from 75 to 150 microns. The same fertiliser treatments and applications were used in the leaching column experiment.

A complete liquid fertiliser solution (excluding P) was applied to 40 litres of demineralised water once at the beginning of the experiment to ensure that P was the only element limiting yield (see Table 4.3). The pots were watered for 11 hours per day (i.e. 7 am to 6 pm) for 30 min per hour and aerated 24 hours per day. The experiment contained six runs, with each treatment replicated three times and applied to each tank once to reduce any influence from slight differences in equipment and position within the glasshouse.

Table 4.3 Basal nutrient solution mixture composition applied to hydroponics experiment.

Basal nutrient solution in milligrams per element applied to each hydroponic tank before the start of each experiment run. The mixture was applied in two parts because its chemical analysis would cause precipitation of the elements if contained within a single part. The solution is modified from Marschner (2012) to remove phosphorus.

Element	Amount applied to each tank (mg)
Boron	13
Calcium	4797
Copper	5
Iron	80
Magnesium	1461
Manganese	35
Nitrogen	79
Phosphorus	0.07
Potassium	7007
Sodium	131
Sulphur	1753
Zinc	6

The demineralised water, basal nutrient solution and dissolved P fertiliser were pumped on the surface of the pots facilitating flow through the growth medium and recycling within the system. The pH and electric conductivity (EC) were checked three times per week throughout the experiment and adjusted to a target pH of 6.5 in water (H_2O) and EC of 1.4 dS/cm. Water samples were taken four times during the experimental run of 21 days, at the begin of each week and the end of each run and subsequently analysed to determine P concentration (mg/L). The shoots of clover and ryegrass were harvested at the end of each run, dried, weighed, and then analysed for P concentration. Analysis for concentrations of P content in dry matter was conducted by bulking the replicates together.

4.2.2 Leaching column experiment

The design contained three replicates of six fertiliser treatments comprising SSP, LWSSP, MCP, DCP, TCP and a nil-P control. The fertiliser was ground and sieved to 75–150 microns to ensure equivalent particle sizes for all treatments. Polyvinyl chloride pots (152 mm diameter, 400 mm deep) were packed with perlite Table 4.4 to a total volume of 6 L.

Table 4.4 Analysis of perlite used in both hydroponics and leaching column experiments.

The critical chemical and physical properties of perlite relative to experimentation on phosphorus in hydroponics and leaching columns.

Analysis	
pH (1:5 perlite:0.01 M $CaCl_2$)	6.7
Bicarbonate-extractable P (Colwell 1965) (mg/kg)	4
Phosphorus buffering index	5.4
EC (dS/cm)	0.042

The columns were pre-leached with the equivalent of 164 mm of rainfall using demineralised water. Phosphorus treatments were applied at a rate equivalent to 120 kg P/ha to the surface of the columns as a single application at the beginning of the experiment. The columns were watered three times per week with 1.5 litres (equivalent to 84 mm of rainfall) of demineralised water and allowed to drain for a minimum of 48 hours between watering, throughout the four-week experiment. Leachate from the columns was collected in a clear plastic bag enclosing the base of the column. The total cumulative rainfall of 924 mm was designed to mimic above average annual rainfall at Mandurah (660–990 mm) on the SCP (Hanson and Foster 2012).

The rate of P leaching was measured by collecting leachate samples after each simulated rainfall event and analysed for total P (mg/L). The leachate collected was stirred and a sample taken, the bag was then emptied and replaced beneath the column. Residual undissolved mg P kg, determined post-experiment was analysed by removing the perlite from the column and sieving it into 3 fractions from the upper 90% of the column (> 2.2 mm, < 2.2–4 mm and > 4 mm). The remaining lower 10% was analysed for P (mg/kg), and the weights of these samples were recorded.

4.2.3 Analysis of data

Refer to Section 3.10 (Statistical analysis, calculations and data storage) for a detailed description of analysis.

4.3 Results and Discussion

4.3.1 Hydroponics Experiment

The dry matter yield of the clover shoots at 42 days after sowing was increased with the addition of P treatments compared to the control (i.e. nil-P) treatment (See Figure 4.1). Since all phosphate forms (MCP, DCP, TCP, SSP and LWSSP) are available to plants when in solution, dry matter yield of clover was increased by the addition of MCP (1.08 g/pot) and DCP (1.00 g/pot) treatments.

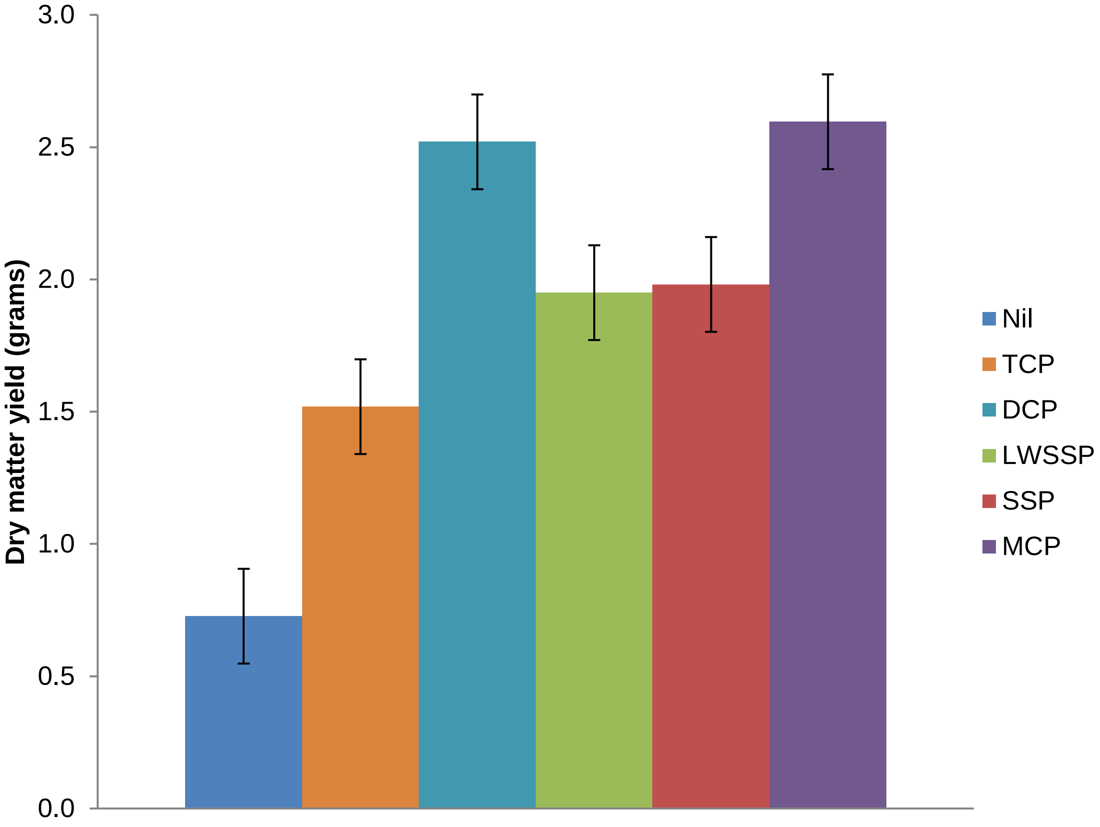


Figure 4.1 The effect of phosphate form on average dry matter yield (g/pot) of clover shoots 42 days after sowing. Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), low water-soluble phosphate (LWSSP) and single superphosphate (SSP). Error bars indicate the least significant difference for comparing phosphate forms between treatments (lsd = 0.36).

The dry matter yield of ryegrass shoots at 42 days after sowing Figure 4.2 was similar to the clover with a significant increase in dry matter yield for all P treatments applied compared to the control (i.e. nil-P) ($p < 0.05$). The dry matter yield of ryegrass for MCP was the same for clover, indicating that when P is not limited in solution, maximum plant growth is achieved. There was a significant increase in dry matter yield of ryegrass shoots in the TCP treatment compared to the clover yield. When TCP is applied to ryegrass, its yield was similar to that in the DCP, LWSSP and SSP treatments however the clover yield from TCP is significantly reduced compared to these treatments. The two species also differed in the nil-P control treatment with ryegrass producing more dry matter yield than the clover dry matter yield. Ryegrass dry matter yield more closely follows phosphate solubility than clover. The increased growth could be due to its more fibrous root systems with an increased volume to allow access to more P from solution (Lynch 1995).

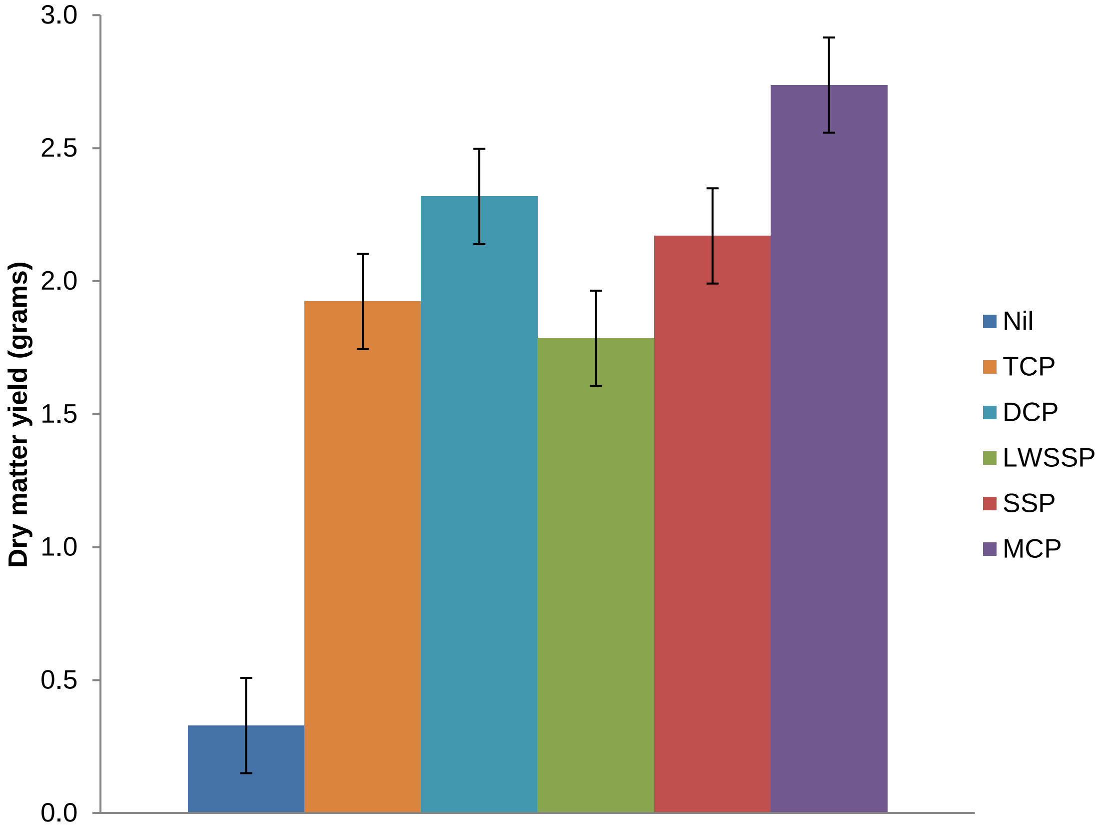


Figure 4.2 The effect of phosphate form on average ryegrass shoot dry matter yield 42 days after sowing for each phosphate form. Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). Error bars indicate the least significant difference for comparison between phosphate forms between treatments (lsd = 0.36).

Changing the pasture composition to include a greater percentage of ryegrass would increase dry matter yield, P use efficiency and reduce P loss to leaching (Bolan *et al.* 1987). There was no significant difference between the yield of clover and ryegrass, and hence the data has been combined and summarised. There is no significant difference between SSP and LWSSP for P use efficiency with both plants species using 45% of the P applied. These results are consistent with research from Price (2006) who indicated that only a certain amount of early P is critical for early plant development. Reducing the solubility by changing the chemical analysis of SSP Table 4.5 to LWSSP did not reduce the dry matter yield or the amount of P taken up by the plants.

The uptake of P by clover is outlined in Figure 4.3 and for ryegrass in Figure 4.4. Phosphorus uptake indicates that P is required early for plant growth and that if it is limiting, then the amount of P that is available will be concentrated within dry matter and restrict growth. As P is assimilated into the plant, it is removed from the solution with the amount of P that is available dependent upon the solubility of each treatment. The concentration of P in the initial solution was adequate for plant growth for all treatments except TCP and the nil-P control increases between weeks 1 and 2 (see Figure 4.5). As P is used for plant growth the concentrations of P in solution, then decline for all treatments except TCP and the nil-P control between weeks 2 to week 4. As the concentration of P in solution increased, the dry matter yield increases. The relationship between P availability and dry matter yield was more correlated for ryegrass.

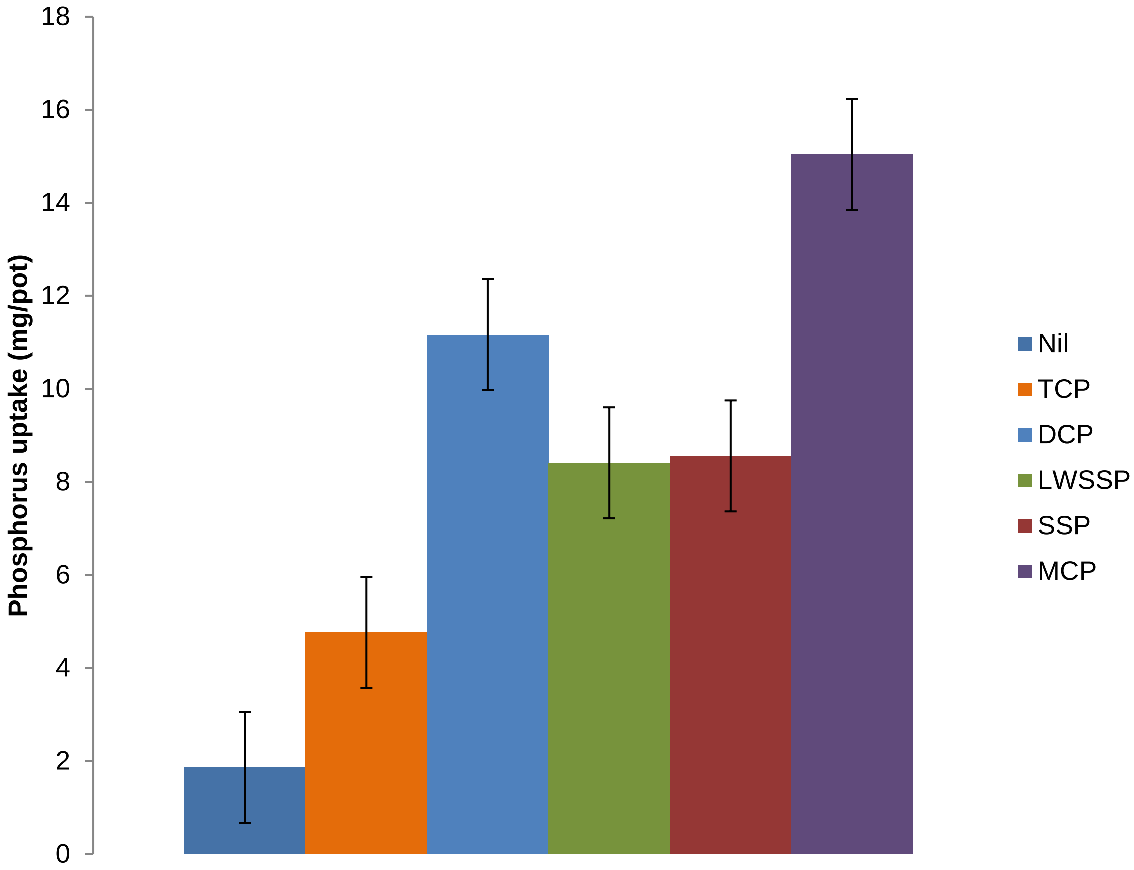


Figure 4.3 The effect of phosphate form on average clover shoot phosphorus uptake 42 days after sowing. Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). Phosphorus per pot concentrations was calculated by (phosphorus tissue (%) multiplied by plant dry matter weight grams) multiplied by 10. Error bars indicate the least significant difference for comparison between phosphate forms between treatments (lsd = 2.385).

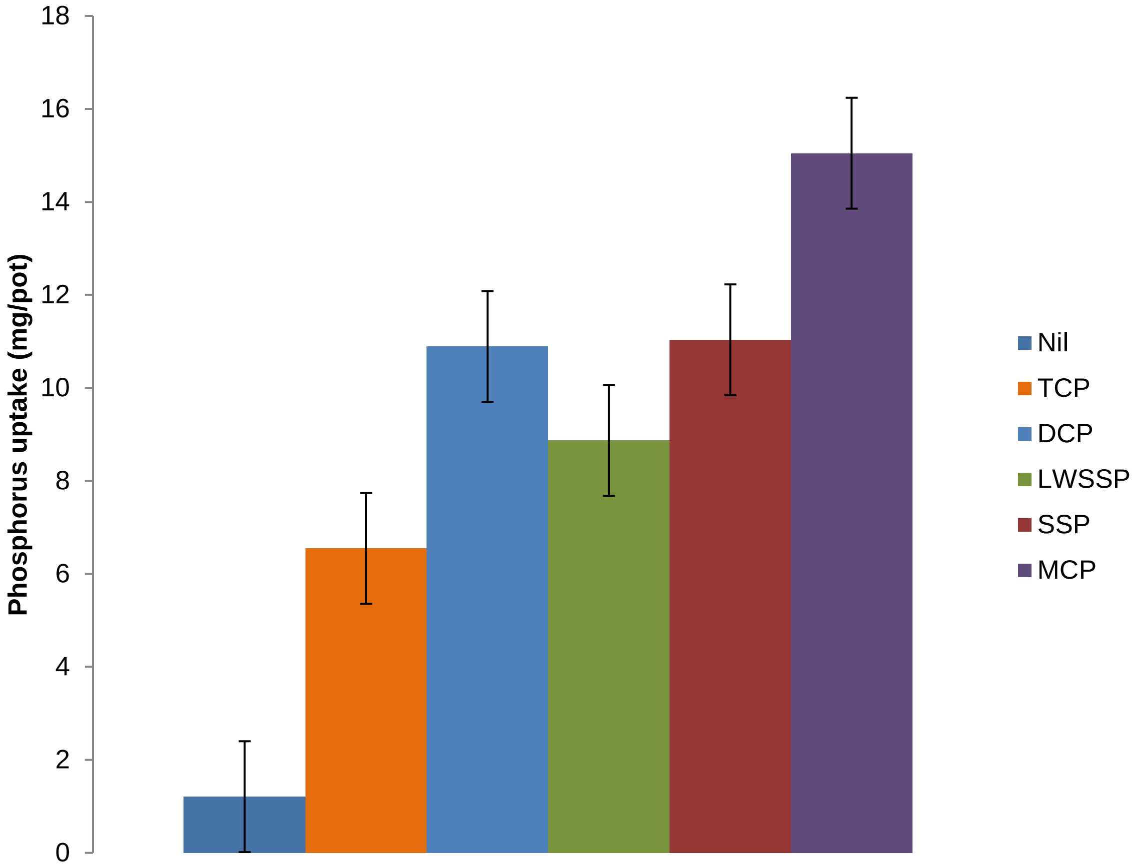


Figure 4.4 The effect of phosphate form on average ryegrass shoot phosphorus uptake 42 days after sowing. Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). Phosphorus per pot concentrations was calculated by (phosphorus tissue (%) multiplied by plant dry matter weight grams) multiplied by 10. Error bars indicate the least significant difference for comparison between phosphate forms between treatments (lsd = 2.385).

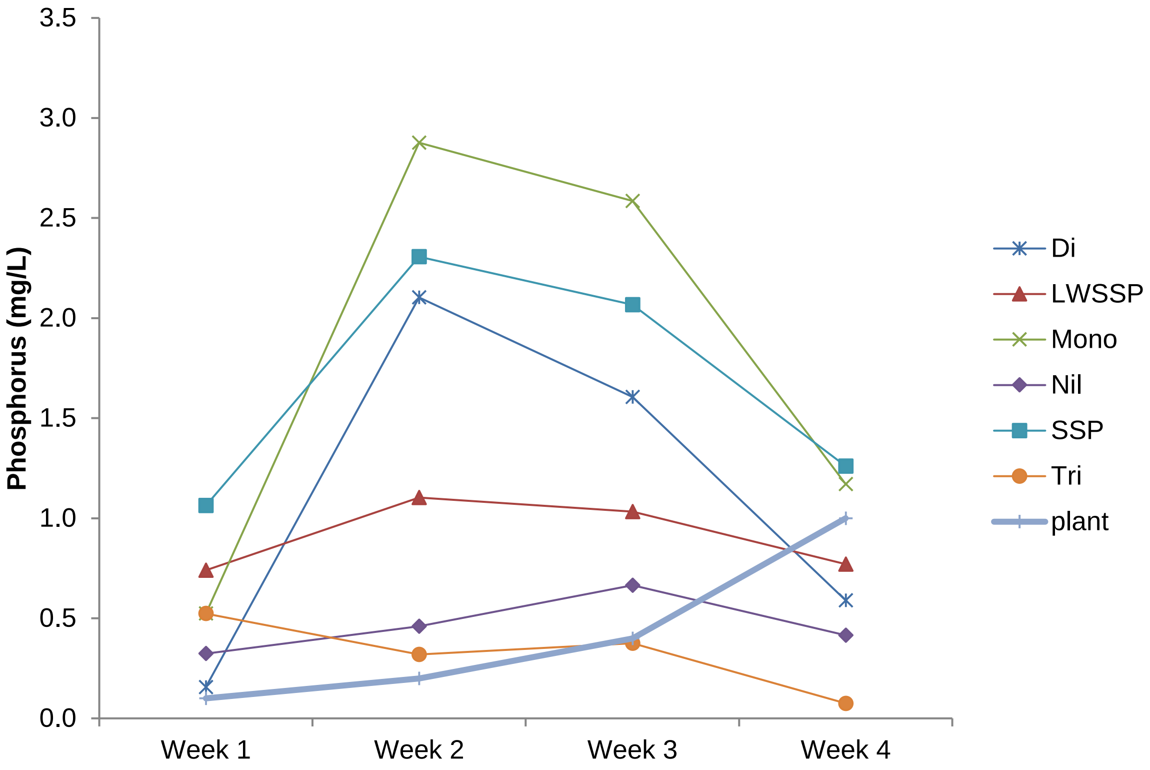


Figure 4.5 Phosphorus concentrations in solution. The concentration of phosphorus in hydroponic solution over the four weeks of the experiment. × monobasic calcium phosphate, □ single superphosphate, Δ low water-soluble superphosphate, * dibasic calcium phosphate, ○ tribasic calcium phosphate, ◊ nil-phosphorus control and + predicted plant phosphorus usage.

Table 4.5 The phosphorus use efficiency of the fertilisers applied to the hydroponics experiment.

The effectiveness of each fertiliser type in the hydroponics experiment is determined by its phosphorus use efficiency, with both clover and ryegrass samples combined based on fertiliser type., Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP), low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). The equation for calculating phosphorus use efficiency is P removed by the plant minus the P uptake nil divided by the amount of P applied, multiplied by 100.

Fertiliser (type)	P removed plant (mg)	P removed plant minus control (mg)	Applied amount of P applied (mg)	PUE (%)
Nil	9.3	0	0	0
MCP	31.9	22.7	16.8	135*
DCP	23.3	14.0	16.9	83
TCP	16.0	6.7	16.8	40
LWSSP	17.0	7.7	17.1	45
SSP	16.9	7.6	17.0	45

* Data is within the experimental sampling error.

The P use efficiency for MCP, DCP and TCP Table 4.5 follows the same trend as the dry matter yield for clover and to a lesser extent the ryegrass with, an increase in solubility translating into increased P uptake in clover and ryegrass. Plants grown with DCP and TCP may have limited access to water-soluble P during the critical early growth stages (< 42 days after sowing) while these forms where dissolving. The results also indicate that all forms of P, once dissolved into water-soluble P, are available to be taken up by plant roots.

4.3.2 Leaching column experiment

Figure 4.5 show that the higher concentration of the predicted water-soluble P, the greater the amount of P is leached under simulated rainfall conditions. Most of the water-soluble P is rapidly leached within the first 84 mm of rainfall (see Figure 4.6).

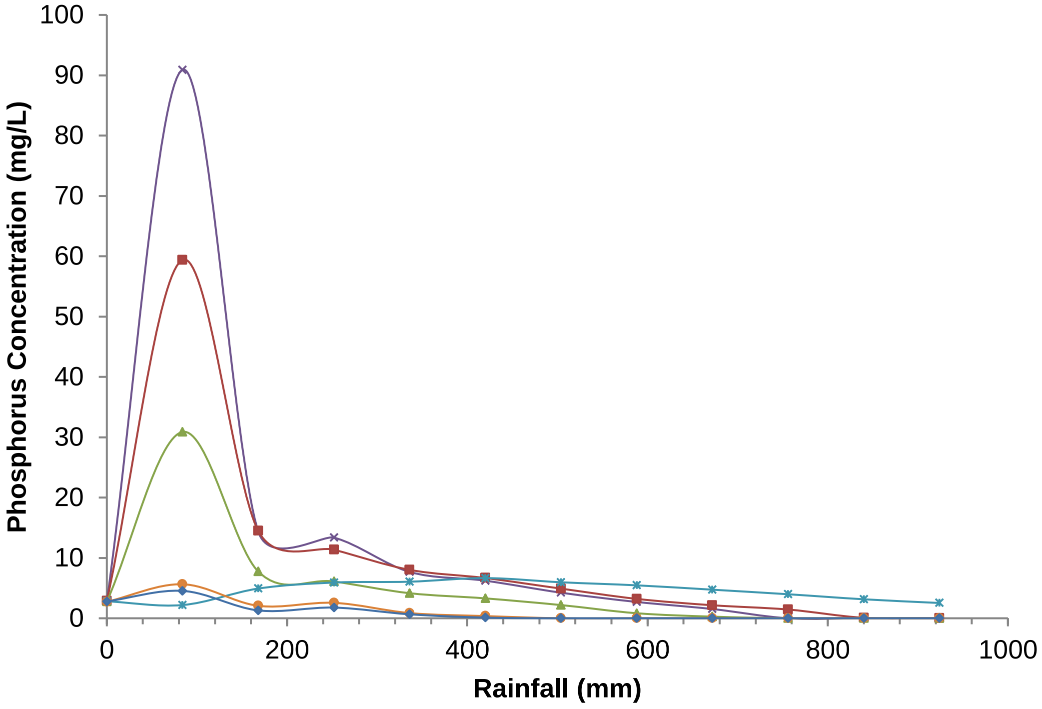


Figure 4.6 Rate of dissolution of phosphate forms. The concentration of phosphorus in the solution applied to perlite in leaching columns following 84 mm of rainfall at each sampling event for a total of 924 mm of rainfall. × monobasic calcium phosphate, □ single superphosphate, Δ low water-soluble superphosphate, * dibasic calcium phosphate, ○ tribasic calcium phosphate, ◊ nil-phosphorus control. The least significant difference for comparing phosphate forms between treatments (lsd = 2.8).

The loss of P through leaching increased with the amount of MCP and was significantly reduced by the relative amounts of DCP contained in each fertiliser Table 4.4 with SSP 86% and LWSSP 35%. The P leaching was the same for DCP and TCP treatment. The leachate concentration for MCP increased to 94 mg P/L, SSP to 62 mg P/Land LWSSP to 34 mg P/L after the first 84 mm of rainfall, which indicates that high water-soluble P fertilisers are very susceptible to early loss from leaching under normal rainfall events. The total cumulative rates at which each P form dissolves follows the trends indicated by the concentrations Figure 4.7 with most of the MCP leaching during the first 84 mm of rainfall, DCP dissolves at a constant rate and TCP dissolved at a very slow rate comparable to the nil-P control treatment (see Figure 4.7).

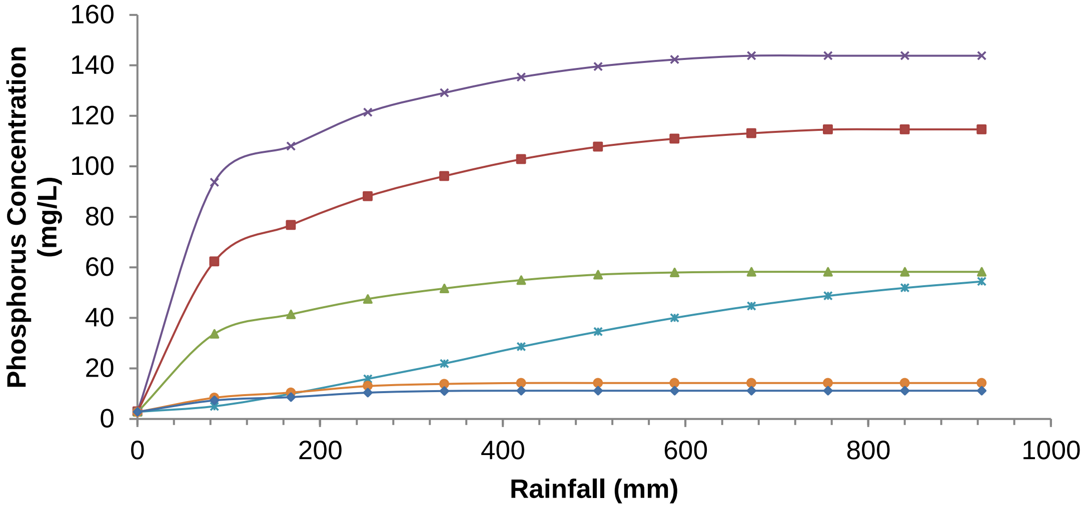


Figure 4.7 Phosphate forms cumulative rate of dissolution. The cumulative amount of phosphorus dissolving in perlite in leaching columns following 84 mm of rainfall at each sampling event for a total of 924 mm of rainfall. × monobasic calcium phosphate, □ single superphosphate, Δ low water-soluble superphosphate, * dibasic calcium phosphate, ○ tribasic calcium phosphate, ◊ nil-P control. The least significant difference for comparing phosphate forms between treatments (lsd = *5.5*).

The rate at which SSP and LWSSP dissolves into solution is consistent with their chemical composition Table 4.3, with the increase percentage of DCP and TCP requiring an increase in the relative amount of rainfall to dissolve them. The leaching of P in the MCP treatment is significantly higher than the other P treatments containing MCP. This indicates MCP contained within SSP and LWSSP dissolved into solution at the same rate. Low water-soluble superphosphate solubility indicates that the MCP component initially dissolves rapidly (0.40 mg P/L/mm) after 84 mm of rainfall and then there is a slower release of its DCP component. The DCP content of LWSSP released at a constant rate approximately of (0.05 mg P/L/mm). The TCP component of LWSSP content dissolves into water-soluble P at a slower rate and is not significant when compared to the nil-P control dissolving at approximately (0.003 mg P/L/mm).

Most of the P leached in the MCP treatment accrued within the first 84 mm of rainfall and if it was applied in April, may have been lost soon after germination (see Appendix 9.3.4.3). Plants may have limited access to applied P fertiliser after two months because the P is leached below the rhizosphere, which is consistent with (Weaver *et al.* 1988). This rate of P loss to leaching assumes that all applied P will completely dissolve to water-soluble P with the addition of subsequent rainfall events.

This relatively slow rate at which TCP dissolves makes it ineffective as a P fertiliser for pasture production. If it is assumed that 100% of MCP dissolves after 924 mm of rainfall (132 mg P/L) and that DCP and TCP will dissolve at a constant rate, it will take approximately four times more rainfall for DCP and 1000 times more rainfall for TCP to dissolve to the equivalent amount of P as a water-soluble P plant available form. Consequently, the reduced rate that DCP dissolves to water-soluble P will allow it to be accessed by plants before it leaches into the environment. The reduction in solubility from SSP and LWSSP, and then constant release of P from DCP provides a P source that is available to plants after the initial plant requirement is provided by MCP.

4.4 Summary

The results indicate that there is a significant reduction in leaching from LWSSP when compared with SSP and this is because of increased percentage of DCP. There is no significant difference in dry matter yield or plant P uptake between LWSSP and SSP, which indicates that they are equally as effective for plant production under hydroponic non-soil conditions. Therefore it can be concluded that the chemistry of LWSSP will allow adequate P to enter in the solution pool for initial plant requirements early in plant growth via the MCP form and then DCP is soluble enough to maintain adequate P solution pool over an extended period with subsequent rainfall events

Plant growth is influenced by the amount of P in the solution pool and this is characterised by the solubility of the phosphates forms as discussed in Section 2.25. Plants utilise increased amount of P (dry matter versus plant P uptake concentrations when P is available within the solution pool. In situations where P is limited in the solution pool, P uptake is decreased. This is reflected in the reduced dry matter yield and plant P uptake. As such it is critical that adequate levels of P be maintained in the solution pool as described in Section 2.4.3.

The hydroponic experiment of this nature created a large P solution pool that is available to the plant. However, when P is present as an insoluble phosphate form (i.e. TCP), this will limit the amount and rate of P entering into the solution pool regardless of the size of solution pools. Both ryegrass and clover have the same requirement for water-soluble P and also dry matter yield, and plant uptake followed the same trend as described in Section 2.4.1. The solubility of TCP even 40 litres of water or above 900 mm of simulated rainfall still did not dissolve into the solution to match plant requirements and resulted in significantly reduced dry matter yield and plant uptake for both species.

Under simulated rainfall conditions, each phosphate form or combination of phosphate forms required a significantly different amount of rainfall to dissolve into solution (see Figure 4.7). This indicated that MCP is highly soluble, DCP is relatively soluble and TCP is insoluble. Through the reduction in phosphate solubility from MCP to DCP in LWSSP, the amount of P in the solution pool will be maintained over a longer period. However, if the phosphate form is too insoluble (i.e. TCP) then the amount of P in the solution pool is reduced, and plant dry matter yield is limited. The ideal situation is to match the phosphate form or combinations of phosphate forms to the size of the solution pool and the rainfall conditions. For example, the LWSSP fertiliser has an increased amount of DCP that dissolves at a slower rate that enables P to go into solution over a long period and remain within the rhizosphere for the plant to access.

CHAPTER 5 GLASSHOUSE EXPERIMENT

5.1 Introduction

The soil types of the SCP in the south-west of Western Australia include heavy clays, duplex soils and deep sands, with the majority being deep sand. These sandy soils have a coarse texture, very in depth, and often are overlaid with an impermeable layer of clay or ironstone (Bolland 1998). The SCP has a dry, temperate climate with hot, dry summers and cold, wet winters and a long-term average annual rainfall of greater than 800 mm, most of which falls during April to October (Hanson and Foster 2012). Nitrogen the predominately infertile sandy soils of the SCP, applying single superphosphate (SSP) fertiliser is the traditional practices for maximising the growth of pasture production.

The dominant pasture combination species on the SCP is Dalkeith subterranean clover and Wimmera annual ryegrass (Price 2006). Annual applications of up to 18 kg/ha of phosphorus (P) were previously recommended to maximise the growth of these pasture systems (Weaver *et al.* 1988). This rate of P application was determined through soil and tissue analysis, taking into account the soil type, background P levels and the soil's ability to retain the applied P (Singh and Gilkes 1991). The combination of relatively high rainfall on the SCP and its sandy soils has resulted in a system that has a low ability to retain nutrients, with nutrients from fertiliser applications being lost to the environment through leaching into waterways (Cox *et al.* 2007).

After soluble phosphate fertilisers are applied to the soil, a series of reactions occur between the soil constituents and the non-P components, including adsorption, desorption, precipitation and dissolution (Shen *et al.* 2011). The applied phosphate can then be adsorbed from solution by the soil, hence reduced the amount of plant-available P (Barrow 1973). The capacity of the soil to adsorb P is determined by the sorption and soil chemistry (Barrow 1999; Damon *et al.* 2014a). The reactions of sorption are highly influenced by the mineralogy and chemistry of the soil, and these influences are greatest on P availability when the soil sorption capacity is high (Damon *et al.* 2014a). Therefore, as soil's ability to absorb P increases, the application rate of P must be increased to overcome the adsorption (Barrow 1975).

A study by Barrow (1975) on the SCP, using 11 soils indicated differing ability to adsorb P were sown with Dalkeith subterranean clover (*Trifolium subterranean* L.) or Wimmera ryegrass. Single superphosphate (SSP) was applied at 4 rates: clover at 2, 4, 6 and 8 g/pot and ryegrass at 0.5, 1, 1.5 and 2 g/pot. Response curves were fitted, and it was determined that ryegrass requires less P 1 g/pot rather than 4 g/pot for clover to attain optimum growth.

The particle size of P fertiliser correlates with the rate at which P dissolves and becomes plant available (Williams and Lipsett 1968). As the particle size of SSP decreases the rate at which the P enters solution increases. This was outlined by Williams and Lipsett (1968), where subterranean clover was grown on four soil types under non-leaching conditions. Clover dry matter yield on the four soils differed by 12% to 25% because of the differences in SSP particle size. This difference in dry matter yield was attributed to both the spatial distribution and rate of solubility of different granule sizes (Williams and Lipsett 1968). Single superphosphate and LWSSP both have a particle size range of 1 to 5 mm which should counter this effect. This range of particle sizes within a fertiliser means that a large granule will be less soluble, dissolved at a decreased rate.

The increasing cost of P fertilisers and stricter environmental regulations means there is a need to increase P use efficiency from fertiliser applications (McLaughlin *et al.* 2011). The P use efficiency is described as the amount of P fertiliser that is applied to a pastures system relative to the amount of P taken up by the plant. The formula for calculating P use efficiency is outlined in Equation 5.1 (Johnston and Syers 2009).

Equation 5.1

$$\text{Phosphorus removed} - \frac{\text{Phosphorus removed by the control}}{\text{Amount of phosphorus applied}} * 100$$

Pasture management on the SCP is based on the 4Rs principles as outlined in Section 2.5. The application of P fertiliser to pastures is based on, the soil Colwell (1965), the PBI Sounness (2008) and Moody *et al.* (2013), P requirement of the pasture, rainfall, and the potential dry matter yield.

The widespread application of SSP for pasture production on the SCP region has been responsible for eutrophication (Weaver *et al.* 1988; Bolland and Gilkes 2001). Phosphorus is a primary nutrient for algal growth in the shallow river systems of the SCP and fertiliser usage has contributed to eutrophication in these waterways since

1968 (Engineers 1988; Hodgkin and Hamilton 1993). The widespread application of SSP for pasture production in the SCP region has been responsible for eutrophication (Weaver *et al.* 1988; Bolland and Gilkes 2001). Consequently, a number of possible solutions have been proposed to slow the loss of P and maintain pasture production including, slow-release coatings such as Bauxite residue, responsible fertiliser management, and chemical manipulation of the water-solubility of SSP (Nyborg *et al.* 1996; Summers and Weaver 2008; IPNI 2015).

Converting SSP to a LWSSP version through reaction (or reversion) is well known however it is difficult to manufacture into a commercial product. It is hypothesised that LWSSP will decrease P leaching while maintaining similar plant dry matter yield and P plant uptake when compared to SSP. This experiment aim to compare P solubility, leaching and pasture production characteristics from LWSSP and SSP on three soil types under controlled glasshouse conditions.

5.2 Methods and materials

5.2.1 Glasshouse experiment

The experimental design comprised of three replicates of 27 treatments to give a total of 81 pots comprising three soils types Table 5.1, three fertiliser types (SSP and LWSSP and a nil fertiliser control, and two most commonly grown pasture species on the SCP, Dalkeith subterranean clover and Wimmera ryegrass. The experiment was designed to include pots with no plants (i.e. controls) grown with and without fertiliser applied, to measure the amount of P leached without the interaction of plants. The pots were randomised in a replicated block design over three glasshouse benches.

Table 5.1 Locations of the three soil collection sites used in the experiment.

The light, medium and heavy soils used in this experiment were collected from 0–10 cm at three locations around Pinjarra and Serpentine, Western Australia on the Swan Coastal Plain. The latitude and longitude of these locations are outlined in this table in degrees, minutes and seconds.

Soil type	Longitude (south)	Latitude (east)
Light	32° 22′ 418″	115° 56′ 981″
Medium	32° 47′ 930″	115° 53′ 642″
Heavy	32° 40′ 586″	115° 48′ 062″

Phosphorus was applied as SSP or LWSSP at rates of 25 kg P/ha and a size fraction of 2–4 mm was used to reduce variation due to particle size differences. The P treatments were applied to the surface of the pots at a rate of 0 fertiliser, 0.37 g/pot of SSP and 0.40 g/pot of LWSSP. Urea and liquid ammonium nitrate were applied to the experiment to ensure N was not limiting. Twenty-seven polypropylene pots (130 mm diameter, 135 mm deep) were packed with each of the three soil types (see Table 5.2).

Table 5.2 Soil properties of pot experiment soils.

The physical and chemical properties of the three soils relevant to this experiment are outlined in this table. These results are an average of three samples unless stated soils before fraction (0–10 cm).

Chemical and physical analysis	Light	Medium	Heavy
pH (1:5 soil 0.01 M $CaCl_2$)	4.6	4.5	4.9
Bicarbonate-extractable P (Colwell 1965) (mg/kg)[A]	10	23	70
Phosphorus binding index (Allen and Jeffery 1990b)	9	16	123
Clay %[B]	3.91	5.01	33.06
Silt %[B]	< 0.01	2.03	7.24
Sand %[B]	96.09	92.96	59.70

[A] Single sample.

[B] CSBP Limited lab numbers SVS15173 – SVS15175.

The light and medium soils were air dry and screened to 2.2 mm and the heavy soil was oven dried and screened to 2.0 mm. The pots were packed with 1.4 kg of light or medium soil) and 2.0 kg of heavy soil. The light soil is coarse, acidic (pH 4.6 $CaCl_2$) and has a low capacity to retain P. The medium soil has a sandy duplex mixture with a moderate capacity to retain nutrients, and the heavy soil had smaller particles, a clay mixture and a high capacity to retain P. The pots were watered with 50 mm of de-mineralised water to bring them to field capacity (see Appendix 9.3.3) and then a basal nutrient mixture was applied (see Table 5.3).

Table 5.3 Basal nutrient mixture composition applied to experiment.

Basal nutrient mixture applied to each pot before the start of and three regular intervals during the experiment. The mixture was applied in a three parts mixture because its chemical analysis would cause precipitation of the elements if it were contained in a single nutrient solution. The solution is modified from Marschner (2012) to remove phosphorus.

Nutrient	Amount applied to soil (mg/kg) per application
Boron	0.12
Calcium	40.97
Chlorine	98.41
Cobalt	0.11
Copper	0.51
Potassium	88.69
Magnesium	3.95
Manganese	3.26
Molybdenum	0.08
Phosphorus	< 0.05
Nitrogen	33.30
Sulphur	34.18
Zinc	2.05

The pots sown with Dalkeith subterranean clover were inoculated with rhizobia to ensure clover nodulation. The clover and ryegrass were thinned to 10 plants after 7 days and misted with de-mineralised water daily before the P fertiliser was applied to ensure uniform plant growth.

The pots were watered four times per week to a total of 100 mm per week (weeks 1–7) and 50 mm per week (weeks 8–11). The total simulated rainfall represented a total of 900 mm which is an above average rainfall typically of 660 mm experienced on the SCP during the growing season (Hanson and Foster 2012). The extra 240 mm of rainfall was applied (after week 11) to simulate above-average leaching conditions.

At 45, 60 and 84 days after sowing, the clover and ryegrass shoots were harvested, by removing all plant tissue one cm above the surface of the pot. Harvested plant matter was dried, weighed and then analysed for P content. The volume of leachate from each pot was measured after every 50 mm of watering and samples were taken to measure the concentration of P (McQuaker *et al.* 1979). After the third harvest (84 days), the roots were extracted from the soil, weighed and then dried before the P concentration was measured.

The P analysis and percentage of MCP, DCP and TCP of SSP and LWSSP are listed in Table 5.3 with the chemistry of MCP, DCP and TCP Table 5.5. The SSP and LWSSP is a commercially manufactured product supplied by CSBP Limited.

Table 5.4 Phosphorus fertilisers with their composition percentage and phosphorus analysis.

The phosphorus fertilisers used in these experiments with the amount of phosphorus present within each of them and the percentage of each form of phosphate (within the brackets). Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP).

	SSP	LWSSP
Total P	9.1	8.3
Water-soluble^A (MCP)	7.8 (86)	2.9 (35)
Citrate-soluble^A (DCP)	0.8 (9)	3.7 (45)
Citrate-insoluble^A (TCP)	0.5 (5)	1.7 (20)

^{A} Measured by standard (AOAC 1975).

Table 5.5 Chemical form, solubility and chemical structure of phosphate fertiliser derived from rock phosphate.

Monobasic Calcium phosphate is the most soluble and the solubility reduces as the ratio of calcium to phosphorus atoms increases.

Type	Solubility	Chemical analysis
Monobasic calcium phosphate	Water-soluble	$Ca (H_2PO_4)_2 H_2O$
Dibasic calcium phosphate	Citrate-soluble	$CaHPO_4 2H_2O$
Tribasic calcium phosphate	Citrate-insoluble	$Ca_3 (PO_4)_2$

5.2.2 Analysis of data

Refer to Section 3.10 (Statistical analysis, calculations and data storage) for a detailed description of analysis.

5.3 Results and Discussion

There was no significant difference in dry matter yield from either plant species in light or medium soils when no fertiliser was applied. However, there was an increase in clover growth ($p < 0.05$) in the control treatment on the heavy soil Figure 5.1 due to its relatively higher soil P levels (70 mg kg P/ha) adequate to sustain initial plant growth. There was no significant difference in the growth of ryegrass controls in any of the three soil types Figure 5.1, which may be explained by ryegrass requiring less P for growth (Barrow 1975). The plant P uptake is outlined in Figure 5.2. In a study by Barrow (1975) on the SCP, using 11 soils of differing ability to adsorb P was sown with Dalkeith subterranean clover or Wimmera ryegrass. Single superphosphate was applied at 4 rates; clover at 2, 4, 5, and 8 g/pot and ryegrass at 0.5, 1, 1.5 and 2 g/pot. Response curves were fitted, and it was determined that ryegrass required less P 1 g/pot than clover 4 g/pot for optimum growth.

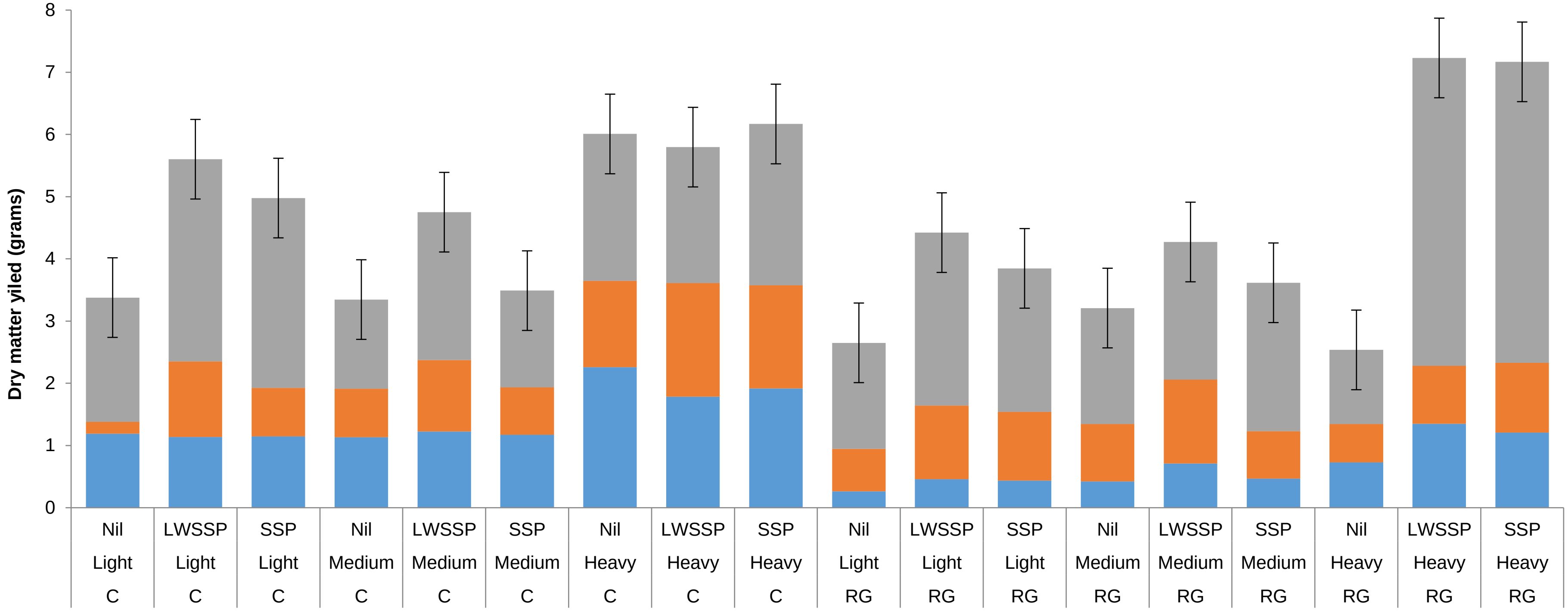


Figure 5.1 Cumulative total dry matter yields (g/pot) of clover and ryegrass from the combined three harvests on the three soil types. The order of fertiliser treatment from left to right is nil-P control, low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). Clover (C) and ryegrass (RG). Error bars indicate the least significant difference for comparing phosphate forms between treatments (lsd = 1.28). The dry matter yield data is stacked with the first harvest at the bottom indicated in blue, the second harvest in the middle indicated in red and the third harvest at the top indicated in green.

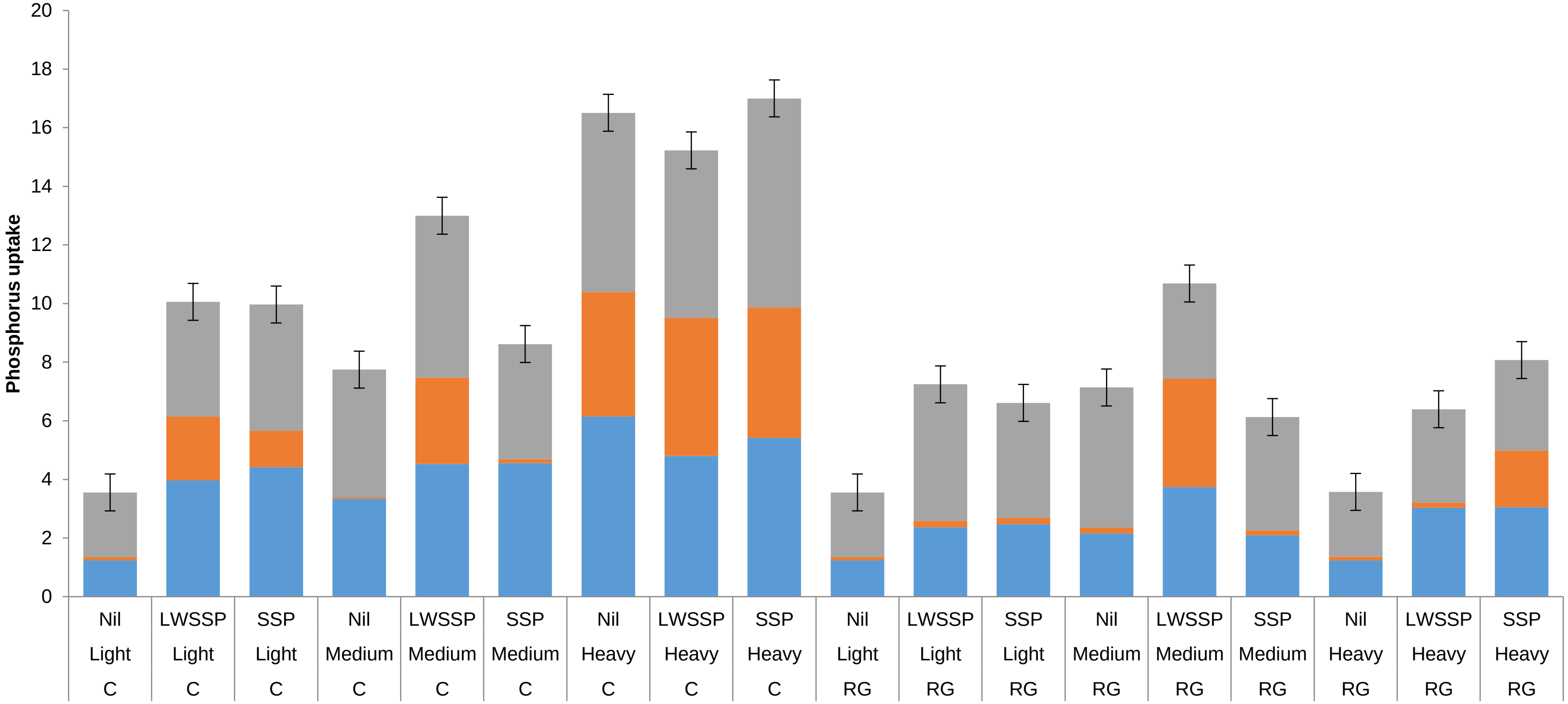


Figure 5.2 Total phosphorus uptake (mg/pot) of clover and ryegrass from the combined three harvests on the three soil types. The order of fertiliser treatment from left to right is nil-P control, low water-soluble superphosphate (LWSSP) and single superphosphate (SSP). Clover (C) and ryegrass (RG). Error bars indicate the least significant difference for comparing phosphate forms between treatments (lsd = 1.26). The phosphorus uptake data is stacked with the first harvest at the bottom indicated in blue, the second harvest in the middle indicated in red and the third harvest at the top indicated in green.

Applying LWSSP increased the dry matter yield of ryegrass compared to the nil-P treatment in the light and heavy soils. The increase in dry matter yield of both species for LWSSP under leaching conditions is due to the reduced solubility of the DCP component, which P dissolves at a slower rate than the MCP, giving plants greater access to P before it is lost to leaching (Chapter 4). The ability of heavy soils to retain more applied P means that regardless of the nature of the fertiliser applied, the rate of leaching of water-soluble P is relatively low (< 10 mg/L). The dry matter yield of the clover significantly increased with the application of LWSSP on the light and heavy soil when compared to the medium soil.

There was no significant difference in dry matter yield when SSP was applied to ryegrass when compared to control P treatment in any of the soil types. For clover, applying SSP significantly increased the dry matter yield when grown on the heavy soil compared to the light and medium soils. There was no significant difference in dry matter yield between the light and medium soils when SSP is applied. These results further support the concept that the heavy soil can retain more P for plant access and, with consistent rainfall more able to hold more moisture for plant growth.

The dry matter yield results in control P treatment show no difference when ryegrass and clover are grown on soil types with increasing phosphorus sorption capacity, with a significant increase in yield of clover grown in the heavy soil. This yield increase may be explained by high levels of available P present (70 mg/kg) Colwell (1965) in the soil before the experiment. In response to LWSSP, compared to SSP, there was no significant difference in dry matter yield of clover or ryegrass on light or medium soils. The P use efficiency of clover increases when LWSSP is applied compared to the SSP and the nil-P for light and medium soils (see Table 5.6).

Table 5.6 Phosphorus use efficiency of clover.

Determining the effectiveness of each fertiliser type was calculated by determining its phosphorus use efficiency based on soil and fertiliser type. The total amount of P removed is the sum of the three dry matter yield harvests. The equation to calculate phosphorus use efficiency was the ((P) removed by the plant subtract (P) uptake nil) divide the amount of (P) applied multiple 100.

Soil	Fertiliser	Tissue P removed (mg/pot)	Tissue P removed minus nil-P (mg)	Amount of P applied (mg)	PUE (%)
Light	Nil	9.6	0	0	0
Light	LWSSP	10.6	1.0	33.1	3
Light	SSP	9.5	-0.1	33.2	0
Medium	Nil	8.4	0	0	0
Medium	LWSSP	14.7	6.3	33.1	19
Medium	SSP	9.4	1.0	33.2	3
Heavy	Nil	16.0	0	0.0	0
Heavy	LWSSP	13.2	-2.8	33.1	0
Heavy	SSP	16.9	0.9	33.2	3

Clover PUE on the medium soil increased from 3% for SSP to 19% for LWSSP. On the heavy soil, this trend is insignificant with the P use efficiency for SSP at 3% and LWSSP 0%. Ryegrass P use efficiency also increases for LWSSP, compared to SSP, for the light and medium soils, and this trend is insignificant on the heavy soil (see Table 5.7). Overall, ryegrass P use efficiency increases for all fertilisers on all soil types.

Table 5.7 Phosphorus use efficiency for ryegrass.

Determining the effectiveness of each fertiliser type was calculated by determining its phosphorus use efficiency based on soil and fertiliser type. The total amount of P removed is the sum of the three dry matter yield harvests. The equation to calculate phosphorus use efficiency was the ((P) removed by the plant subtract (P) uptake nil) divide the amount of (P) applied multiple 100.

Soil	Fertiliser	Tissue P removed (mg)	Tissue P removed minus nil-P (mg)	Amount of P applied (mg)	PUE (%)
Light	Nil	3.7	0	0	0
Light	LWSSP	8.9	5.3	33.1	16
Light	SSP	6.8	3.1	33.2	9
Medium	Nil	5.3	0	0	0
Medium	LWSSP	12.5	7.1	33.1	21
Medium	SSP	6.3	0.9	33.2	3
Heavy	Nil	2.3	0	0.0	0
Heavy	LWSSP	6.9	4.6	33.1	14
Heavy	SSP	7.6	5.3	33.2	16

The P use efficiency results in Table 5.7 indicate that LWSSP is more efficient than SSP for the light and medium soils where more P was lost to leaching. The LWSSP with increased DCP component dissolves at a slower rate, allowing the plant more time to access soluble P before it is lost to leaching. These results suggest that the application of LWSSP is comparable to SSP for dry matter yield on light and medium soil types, but not on heavy soil types. This result may occur because the DCP dissolves at a rate that is non-limiting to both pasture species. It is proposed that LWSSP contains enough MCP for the establishment of the plant's root system and then DCP dissolves at a rate that the plant can access the P later before it leached from the root zone.

The leachate volume was collected for all treatments Appendix 9.3.3.1 with the amount for the controls (nil-P, nil-species) is shown in Figure 5.3. The simulated rainfall was divided and applied 4 times per week with the leachate collected twice per week. The leachate volume collected, and this watering regime indicated that moisture was not limiting for plant production on any soil type regardless of the soil type (light, medium and heavy) and individual water holding capacity. The calculated watering holding capacity is outlined in (see Appendix 9.3.3).

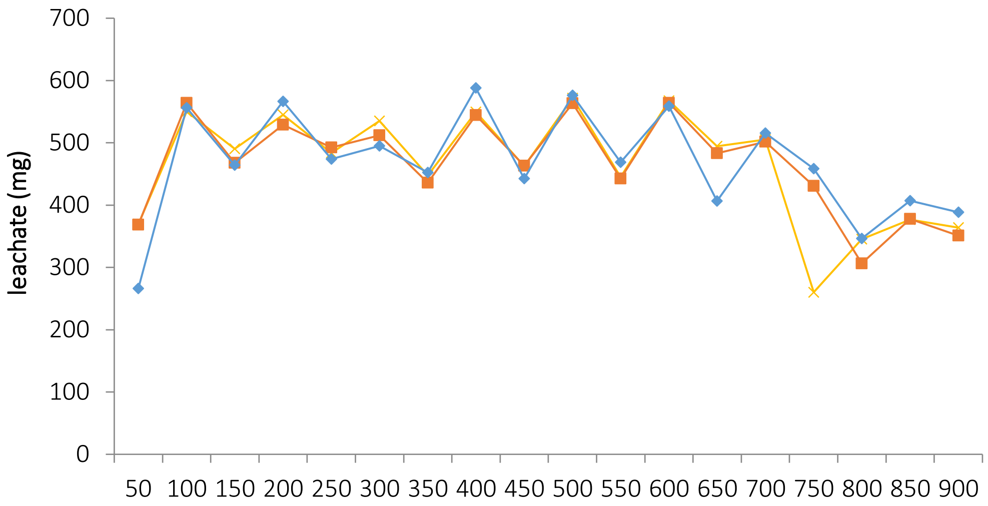


Figure 5.3 Leachate volumes for the nil species for three of the soil types, rainfall, is displayed along the X axis. × light soil, □ medium soil and ◊ heavy soil.

Light soil (PRI = 1.1, PBI = 8.9) was prone to leaching of up to 55 mg P/L (total) after 900 mm of rainfall (see Figure 5.4). Applying SSP and LWSSP to the soil in the absence of plants significantly increased leaching (see Figure 5.4). Growing clover and ryegrass significantly ($p < 0.05$) reduced P leaching from SSP and LWSSP. The uptake of P by plants reduced P leaching as plants removed P from solution before it was lost from the root zone. Plant roots possibly also reduced water infiltration rate and this may have contributed to a reduction in P leaching.

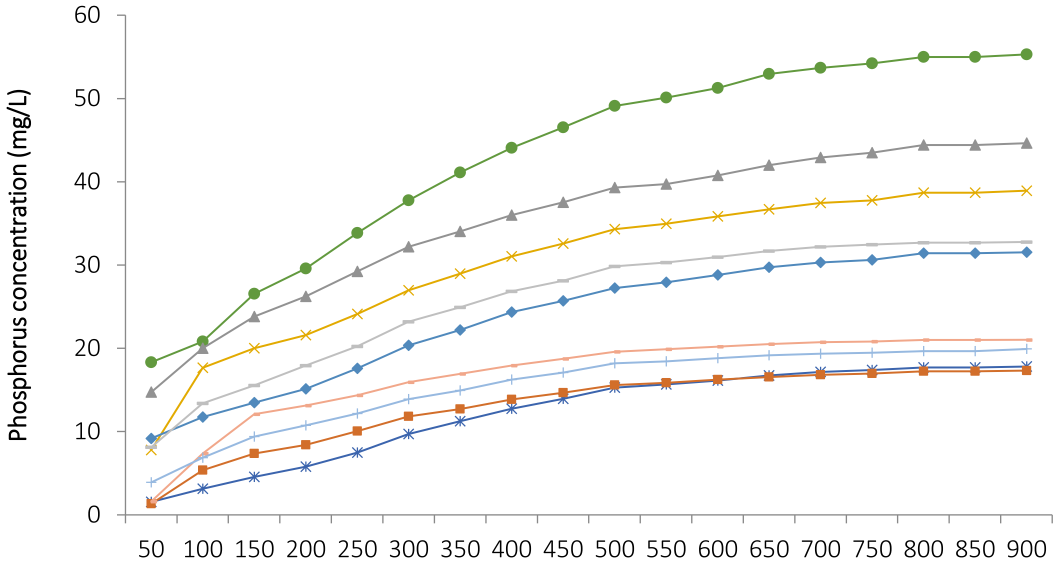


Figure 5.4 Cumulative totals of phosphorus in leachate from the light soil, rainfall is displayed along the X axis. * nil (nil-P), × nil (low water-soluble superphosphate), ● nil (single superphosphate), □ clover (nil-P), ◊ clover (low water-soluble superphosphate), Δ clover (single superphosphate), ○ ryegrass (nil-P), + ryegrass (low water-soluble superphosphate), ─ ryegrass (single superphosphate). The least significant difference for comparing phosphate forms between treatments (lsd = 1.1).

In the medium soil (PRI = 3.7, PBI = 16.4), applying SSP to clover or ryegrass, compared to the control treatments with no plants, significantly increases P leaching with all three treatments accumulating approximately 40 mg/L of P (see Figure 5.5). Applying LWSSP to clover or ryegrass compared to the controlled treatments shows significantly less P leaching. One explanation for this difference is that plant roots, once established, use the dissolved P before it is lost to leaching.

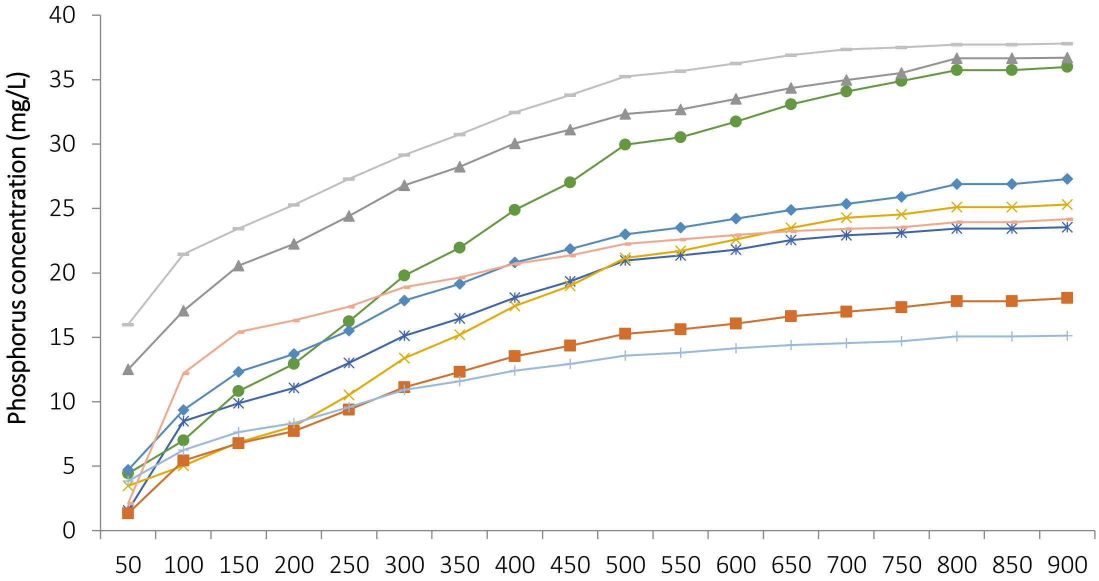


Figure 5.5 Cumulative totals of phosphorus in leachate from medium soil, rainfall is displayed along the X axis. * nil (nil-P), × nil (low water-soluble superphosphate), ● nil (single superphosphate), □ clover (nil-P), ◊ clover (low water-soluble superphosphate), Δ clover (single superphosphate), ○ ryegrass (nil-P), + ryegrass (low water-soluble superphosphate), ─ ryegrass (single superphosphate). The least significant difference for comparing phosphate forms between treatments (lsd = 1.1).

In the heavy soil (PRI = 89.4, PBI = 123.3), the leaching of P was lower than the other soil types with the majority of P leaching within the first 100 mm of rainfall (see Figure 5.6). These results indicate that in high rainfall situations on this heavy soil type, the chances of P leaching are reduced and applying a high water-soluble superphosphate will maximise P availability to plants. This reduction in leaching combined with the plant's requirement for water-soluble P means that LWSSP can be applied as it will not be lost to leaching.

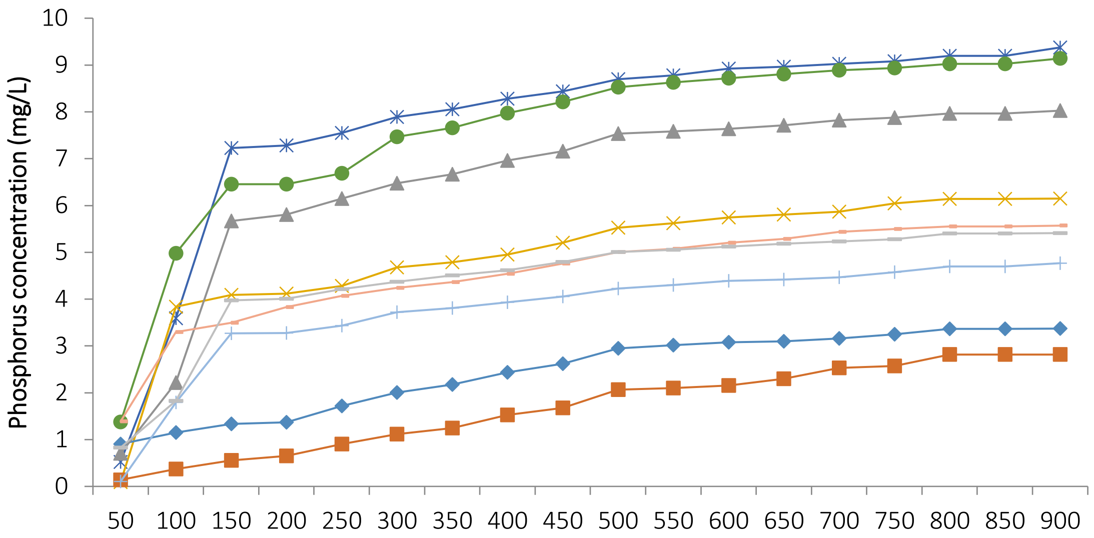


Figure 5.6 Cumulative totals of phosphorus in leachate from the heavy soil, rainfall is displayed along the X axis. * nil (nil-P), × nil (low water-soluble superphosphate), ● nil (single superphosphate), □ clover (nil-P), ◊ clover (low water-soluble superphosphate), Δ clover (single superphosphate), ○ ryegrass (nil-P), + ryegrass (low water-soluble superphosphate), ─ ryegrass (SSP). The least significant difference for comparing phosphate forms between treatments (lsd = 1.1).

As the soil's ability to absorb P increases (i.e. from sand, to loam, to clay), the relative amount of P leaching decreases, given the same rainfall and environmental conditions. In general, under similar rainfall conditions, as the soil's ability to retain P decreases, a P fertiliser should have a greater percentage of DCP to reduce the likelihood of P leaching to the environment.

5.4 Summary

The size of the P solution pool varies depending upon the physical and chemical properties of the soil (see Section 2.2.5, 2.2.6 and 2.2.7). The application of inorganic fertiliser to the soil increases the amount of P within the active pool that can then move into the solution pool for utilisation by the plant. If the solution pool of the soil is relatively small (i.e. based on increased PBI), the applications of large amounts of highly soluble P (MCP) will rapidly fill it up and then the excess soluble P will likely be leached from the rhizosphere (Chapter 4).

Under simulated rainfall conditions of up to 900 mm annually, reducing the solubility of P through increasing the amount of DCP in fertiliser produces a similar dry matter yield and P plant uptake on all soil types. However, increasing the amount of DCP in SSP had a significant reduction of P leaching on all soil types. As the size of the soil solution pool increased, the relative amount of P lost to leaching decreased. This indicates that the amount of DCP within a P fertiliser can be manipulated to match soil properties (i.e. measured using PBI), provide maximum available P to the plant and reduce P loss to leaching. As the PBI of soil increases, the amount of DCP can be decreased and the amount of MCP can be increased. Rainfall also has a significant effect on the amount of DCP within the fertiliser since rainfall is a major influence of soluble P leaching below the plant's rhizosphere.

The SCP sandy soil types that have a low PBI of less than 16 has a limited ability to retain P and contribute to a greater loss of P. Hence, this research recommends that as the soil’s ability to retain P reduces, the relative solubility of P in fertiliser is decreased so that it is released in smaller amounts over a longer period to allow plants access to the pool of soluble P. Soils on the SCP require testing for Colwell P levels and PBI before fertiliser is applied to determine optimum P requirements. In summary, this research shows that the P chemistry (ratio of MCP to DCP) in SSP can be manipulated to reduce leaching losses caused by high rainfall on low PBI soils. Thereby improving pasture growth on the SCP and reducing P contamination of waterways.

CHAPTER 6 FIELD EXPERIMENTS

6.1 Introduction

In 2006 the Western Australian Government proposed that high water-soluble phosphate fertilisers with a phosphorus concentration greater than 40%, would be phased out of environmentally sensitive regions to reduce the impact of fertiliser used in agriculture on the waterways of the SCP in south-west Western Australia (Cox *et al.* 2007). The most common P fertiliser applied to pasture production systems in Western Australia is SSP that is manufactured from rock phosphate and typically has a water-soluble content > 80% (Agriculture 1964; Chien and Menon 1995). Starting in 2009, the phasing out of the higher water-soluble phosphate fertilisers containing a P concentration above 40% was to occur over a period of four years. Phosphorus is a critical element for plant growth and pasture production because it is an essential element for genetic material, cell membranes, energy transfer and cell storage processes (Schachtman *et al.* 1998). The majority of P is needed during the early growth stages, and it must be available in a water-soluble form for plant roots to access (Black 1968; Price 2006).

The soils of the SCP are predominantly sandy and infertile as defined by Moore (2004) and when they are used for pasture production, they require high inputs of fertiliser, commonly SSP (Yeates 1993). These soils have a low ability to retain applied P as defined by Bolland and Allen (2003), therefore fertiliser rates of greater than 15 kg/ha per year of P are normally required. The combination of the low capacity of the soil to retain P, high solubility of the applied fertiliser, and a relatively high rainfall results in excess P discharged into the waterways. These excess nutrients promote algal growth in the shallow river systems of the region, such as the Peel Inlet and Peel Harvey estuary, where large surface areas of algae growth have been occurring since the 1960s (Yeates 1993).

Single superphosphate is comprised of three forms of calcium phosphate, MCP, DCP and TCP in proportions shown in Table 6.3. Tribasic calcium phosphate is considered an ineffective form for pasture production because it dissolves too slowly for plant growth and is only present in SSP as a by-product of the manufacturing process. The chemistry of SSP has been designed to ensure maximum availability to plants but these ratios can be varied in the manufacturing process (Mclean and Wheeler 1964). Each phosphate form differs in solubility, and hence the forms require different amounts of rainfall to become plant available. Tribasic calcium phosphate is regarded as the least effective form for plant uptake because it is very insoluble and thus unavailable to plants.

Many strategies to reduce phosphate leaching from SSP have been tried such as coating bauxite residues onto the granule surface as described by Summers *et al.* (1999a) or changing the soil properties to increase P retention (Summers *et al.* 1993b; Pathan *et al.* 2002). None of these methods has been widely adopted because of cost, practicality or public concern. Consequently, a method to reduce the solubility of P fertiliser while matching plant requirements and overcoming the problems associated with P availability is required. The P cycle can be considered as a simple input and output system with P being added into the system as fertilisers, pasture assimilating the available P for plant growth, and excess P being lost from the system. Reducing the loss of P and maintaining the amount of P that is available to the plant over subsequent seasons is essential for sustainable agriculture.

Edmeades (2000) found that similar dry matter yield responses could be obtained with DCP compared to SSP under certain conditions and proposed that reducing the proportion of water-soluble P in SSP would achieve similar dry matter yield improvements relative to current fertilisers. This change to SSP would enable existing manufacturing equipment to be used without additional alternative approaches, such as a slow-release coating (Nyborg *et al.* 1996; Summers *et al.* 2000). It is possible to reduce leaching and obtain equivalent dry matter yields in the pasture to SSP by reducing the proportion of MCP and increasing the proportion of DCP and TCP. This change in the proportion MCP and DCP would enable a percentage of P to dissolve at a slower rate when applied to the soil but still is retained within the rhizosphere of the plant long enough for the plant to access.

Several fertiliser models have been developed to quantify the amount of P required for growing cereal crops (Speirs *et al.* 2013; Dowling 2015). These models will differ between pasture species and cereal crops because the plant's requirement for P slightly differs for maximum pasture growth (Colwell 1963; Dowling 2015). The pasture requirements for P have been modelled through field and glasshouse experiments (Cornforth and Sinclair 1982; Nguyena and Goha 1992; Ratkowsky *et al.* 1997). A review of required application rate of P for optimum plant growth was outlined by Colwell (1965) and was found to be dependent on soil properties, PBI, and plants requirements to maximise pasture growth has been outlined by (Gourley *et al.* 2007). As a general rule, the critical range of P to maintain plant growth increases the soil's ability to retain applied P increases.

It is hypothesised that LWSSP will be as effective as SSP for pasture production systems under field conditions. It is predicted that under field conditions on lighter soil types (PBI < 20), that increasing the amount of DCP in SSP will produce similar plant dry matter yield, P plant uptake while reducing the loss of P from leaching below the rhizosphere. There is no fertiliser model which has been developed and tested for LWWSP. The objective of this field experiment (Chapter 6), is to test the optimum phosphate chemistry of SSP under field conditions, build on experimental data obtained from the Chapters 4 and 5 and develop a model based on the PBI of the soil and the rainfall. The aims are: (1) compare LWSSP and SSP interactions on pasture production in field conditions by measuring dry matter yield, P plant tissue percentage and soil P levels; and (2) to develop a concept that models how LWSSP can fit into the pasture production system based on rainfall and P buffering index.

6.2 Methods and materials

6.2.1 Field experiments

Two field experiments were conducted, site 1 is north-west of Pinjarra and site 2 is west of Serpentine, Western Australia (see Table 6.1). Both the sites have sandy soils, as characterised as Tenosols (Isbell 1996).

Table 6.1 Location of the field experiment sites.

The two field experiment sites are located on the Swan Coastal Plain of south-west Western Australia. The latitude and longitude of these sites are outlined in this table in degrees, minutes and seconds.

Location	Longitude (south)	Latitude (east)
Site 1	32° 32′ 323″	115° 50′ 596″
Site 2	32° 22′ 264″	115° 55′ 583″

Soil analysis of the field experiments and leaching column experiment was conducted pre (leaching column and field) and post-experiment (field) with the analysis for 0 and 25 kg/ha of P treatments outlined in Table 6.2.

Table 6.2 Soil properties of the field experiments and leaching column experiments.

The relevant physical and chemical properties of the soils at the two experiment sites are outlined in this table. All samples were collected from 0–10 cm depth and the leaching columns were completely filled with the soil. Pre the application of phosphorus fertiliser to the experiment (pre-exp) and post the application of all phosphorus fertiliser to the experiment (post-exp). Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP).

Site 1	**(Pre-exp)**	**(Post-exp)**	**(Post-exp)**	**(Post-exp)**	**Leaching column (Pre-exp)**
Phosphorus rate (kg/ha)	0	0	25	25	0
Fertiliser	-	-	SSP	LWSSP	-
Bicarbonate-extractable P (Colwell 1965) (mg/kg)	3	5	8.5	9.3	4
pH (1:5 soil 0.01 M $CaCl_2$)	4.3	-	-	-	4.4
Phosphorus buffering index (Allen *et al.* 2001)	15	-	-	-	9
Site 2	**(Pre-exp)**	**(Pre-exp)**	**(Pre-exp)**	**(Pre-exp)**	
Phosphorus rate (kg/ha)	0	0	25	25	-
Fertiliser	-	-	SSP	LWSSSP	-
Bicarbonate-extractable P (Colwell 1965) (mg/kg)	12	7.7	6.3	8.4	-
pH (1:5 soil 0.01 M $CaCl_2$)	4.6	-	-	-	-
Phosphorus buffering index (Allen *et al.* 2001)	6.1	-	-	-	-

During this three-year experiment, both sites received rainfall above the average of 660 mm per year, with the majority of the rainfall (i.e. 579 mm) falling during the growing season (April to October) (Hanson and Foster 2012).

The two field experiments had the same experimental design but with different plot randomisations (see Appendix 9.3.4). They contained three replicates of nine treatments to give a total of 27 plots, with the nil-P treatment receiving no added P fertiliser. The plot sizes were 2.5 m by 10 m in 2009 and 2.5 m by 5 m in 2010 and 2011 with both sites divided into two sections using a fence. The two fertilisers treatments (SSP and LWSSP), were applied at 5, 10, 15 and 25 kg P/ha. The recommended application rate of P was determined using a commercial model and, for optimum dry matter yield, with site 1 requires (22 kg P/ha) and site 2 requires (20 kg P/ha). The fertiliser treatments were applied once annually for three consecutive years. The sites were sown to a 50:50 mixture of clover and ryegrass.

Dry matter yield measurements were taken using a rising plate meter method as defined by Earle and McGowan (1979) during the growing season of each year. The meter readings were calibrated with dry matter yield pasture cuts from within quadrats. The pasture was cut to ground level and dried at 75°C in a forced-draft oven for at least 48 hours before being weighed to determine dry matter weights. The dry matter yield at site 1 was measured annually in 2009, 2010 and 2011. The dry matter yield at site 2 was measured three times in 2009, once in 2010 and three times in 2011. Tissue analysis samples were collected from random locations within the plots and this sampling technique was used throughout the experiment. The tissue samples were dried, and the ICP-AES method used to determine the concentration of P in the plant tissue. After each measurement, the fence was moved to the grazed section and cattle allowed to graze on the measured section.

Soil samples at each site were collected using a metal tube, 20 mm in diameter to a depth of 100 mm before treatments were applied. Twenty soil sample cores were collected from random locations within each plot in January and February in 2010 (all treatments), 2011 (treatments, nil-P, 25 kg/ha SSP and 25 kg/ha LWSSP) and 2012 (all treatments). The soil was analysed for bicarbonate-extractable P using an automated version of the Colwell procedure (Colwell 1965). The SSP and LWSSP fertilisers were obtained from CSBP Limited and the analysis is shown in Table 6.3. Granule size ranged from 1 to 5.6 mm.

Table 6.3 Phosphorus fertilisers with their composition percentage and phosphorus analysis.

The phosphorus fertilisers used in these experiments with the amount of phosphorus present within each of them and the percentage of total phosphorus of each phosphate form (within the brackets). Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP). Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP).

Analysis	SSP	LWSSP
Total P (%)	9.1	8.3
MCP (%)[A]	7.8 (86)	2.9 (35)
DCP (%)[A]	0.8 (9)	3.7 (45)
TCP (%)[A]	0.5 (5)	1.7 (20)

[A] Measured by standard (AOAC 1975).

Basel nutrients Appendix 9.1.3 to 9.1.9 were applied throughout the experiment to ensure that P was the only element limiting dry matter yield. Basal nutrients and P fertilisers were applied to the soil surface (granular) at the start of the experiment as is common practice for fertilising pastures in Western Australia.

6.2.2 Leaching column experiment

The experimental design incorporated three replicates of three fertiliser treatments comprising SSP and LWSSP and a nil-P control. The fertiliser granules were sieved to ensure that particles size of P was 1–2 mm for all treatments. Polyvinyl chloride pots (152 mm diameter, 400 mm deep) were packed with sand Table 6.2 to a total volume of 6 L. The columns were pre-leached with the equivalent of 164 mm rainfall using demineralised water. Phosphorus treatments were applied at a rate equivalent to 120 kg/ha of P in a single application at the beginning of the experiment and applied at 5 mm below the surface of the soil. The higher rate of P was selected to maximise leaching properties of the two P fertilisers. The columns were watered three times per week with 1.5 L of water (equivalent to 84 mm of rainfall) and allowed to drain for a minimum of 48 hours between watering throughout the four-week experiment. Leachate from the columns was collected in a clear plastic bag enclosing the column. The total cumulative rainfall of 840 mm was designed to mimic the above-average annual rainfall on the SCP (660–990 mm) (Hanson and Foster 2012). The rate of P leaching was measured by collecting leachate samples after each simulated rainfall event and analysing the total P (mg/L).

6.2.3 Analysis of data

Refer to Section 3.10 (Statistical analysis, calculations and data storage) for a detailed description of analysis.

6.3 Results and Discussion

6.3.1 Field experiment

The dry matter yield of the two field experiments varied because of seasonal conditions and soil properties over the three years. The pasture dry matter yield for site 1 is displayed by year in Figure 6.1–Figure 6.3 and site 2 Figure 6.4–Figure 6.6. The data is stacked with each dry matter yield measurement on top of one another and statistical means displayed as the totals of the year.

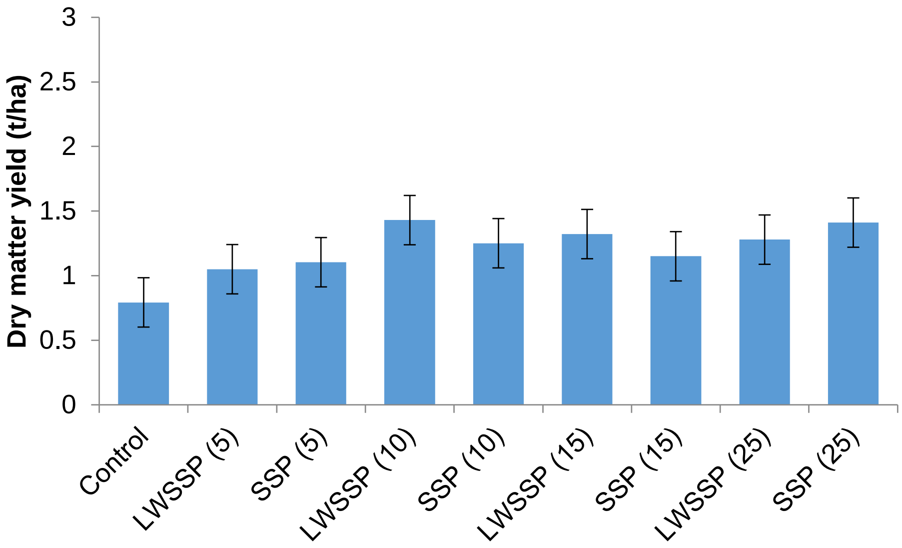


Figure 6.1 Dry matter yield for field experiment site 1 (2009). Total dry matter yield in tonnes per hectare from all measurements combined for each of the five rates of phosphorus applied annually as either control, LWSSP or SSP. Dry matter yield was measured 138 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob = 0.056, lsd = 0.06).

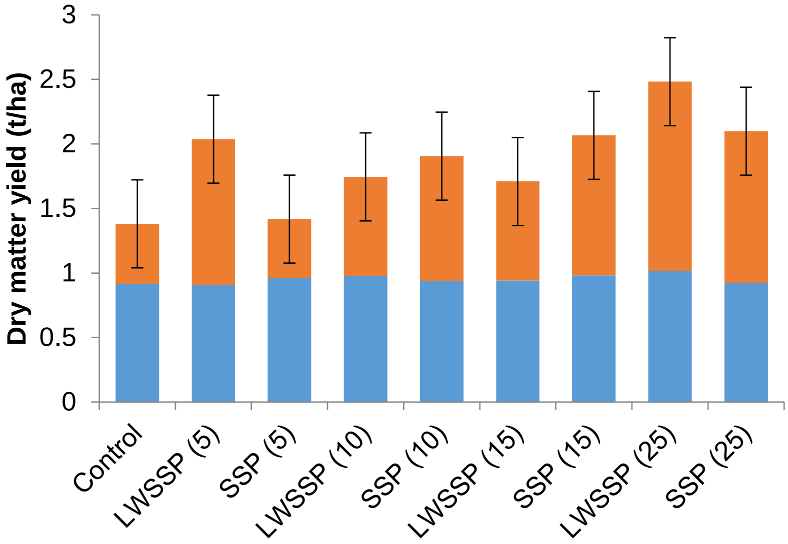


Figure 6.2 Dry matter yield for field experiment site 1 (2010). Total dry matter yield in tonnes per hectare from all measurements combined at the five rates of phosphorus applied annually. Dry matter yield was measured 101 and 151 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob = 0.012, lsd = 0.68).

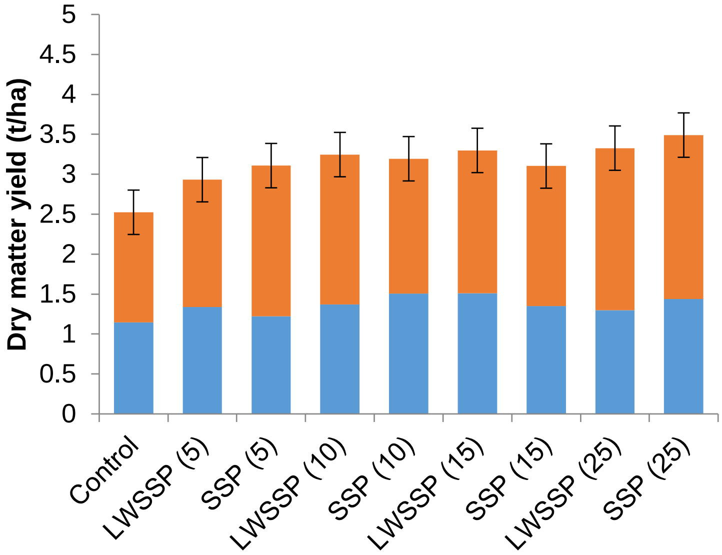


Figure 6.3 Dry matter yield for field experiment site 1 (2011). Total dry matter yield in tonnes per hectare from all measurements combined at the five rates of phosphorus applied annually. Dry matter yield was measured 101 and 165 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob =0.171, lsd = 0.55).

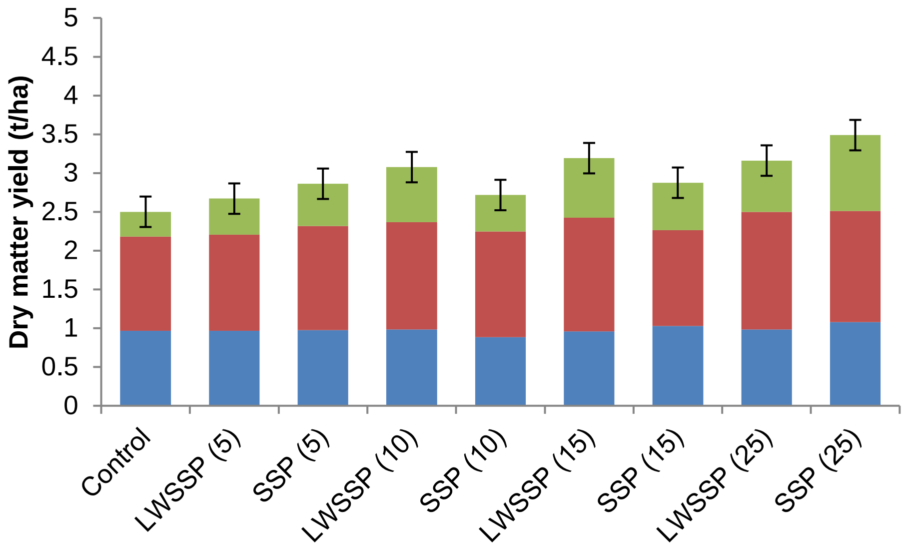


Figure 6.4 Dry matter yield for field experiment site 2 (2009). Total dry matter yield in tonnes per hectare from all measurements combined at the five rates of phosphorus applied annually. Dry matter yield was measured 65, 135 and 155 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob = 0.002, lsd = 0.39).

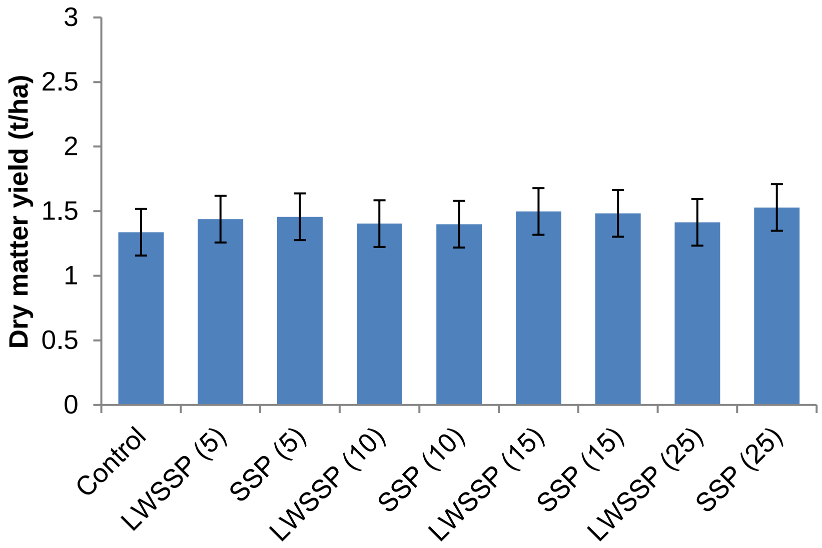


Figure 6.5 Dry matter yield for field experiment site 2 (2010). Total dry matter yield in tonnes per hectare from all measurements combined at the five rates of phosphorus applied annually. Dry matter yield was measured 100 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob = 0.485, lsd = 0.36).

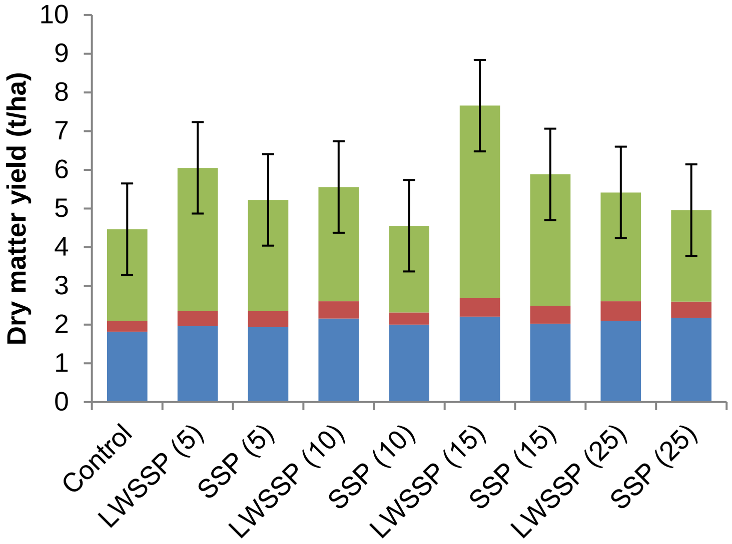


Figure 6.6 Dry matter yield for field experiment site 2 (2011). Total dry matter yield in tonnes per hectare from all measurements combined at the five rates of phosphorus applied annually. Dry matter yield was measured 165, 191 and 217 days after phosphorus fertiliser application. The least significant difference for comparing phosphate forms between treatments (prob = 0.284, lsd = 2.363).

Dry matter yield at site 1 increased every season, from one t/ha in 2009 to 3 t/ha in 2011, with a maximum P application rate of 25 kg/ha. The soil P Colwell (1965) level increased from 3–5 to 8.5–9.3 mg P/kg over three years, which reflects a moderate capacity throughout the growing season Table 6.2 P uptake measurements of the plants were taken for each season and these are shown in Figure 6.7 for site 1 and Figure 6.8 for site 2.

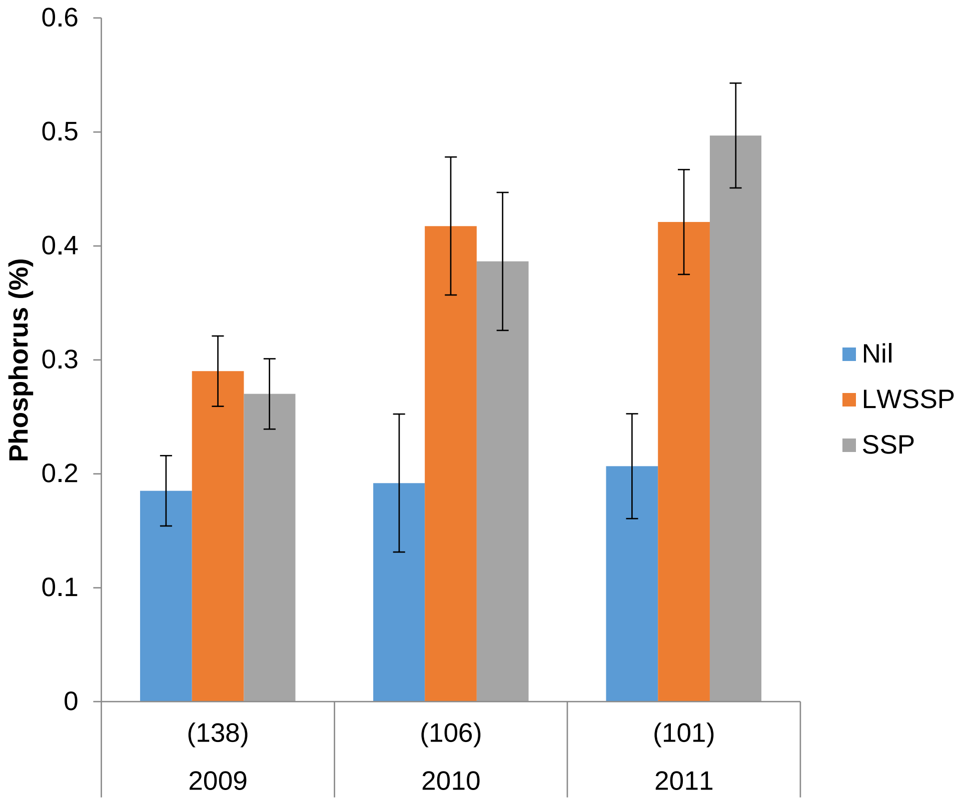


Figure 6.7 Phosphorous tissue analysis of field experiment site 1 for three years, sampled between 101 and 138 days from fertiliser application at 25 kg P/ha. Values in parentheses are days after application of phosphate fertiliser, with the year of sampling below. The samples are concentrations of total phosphorus (%). Nil-P (Nil), single superphosphate (SSP), low water-soluble superphosphate (LWSSP), phosphorus fertilisers were applied at 25 kg/ha of phosphorus. Error bars indicate the least significant difference for comparing phosphate forms between treatments (2009 (138) prob = 0.03 lsd = 0.06, 2010, (106) prob = 0.001 lsd = 0.12, 2011, (101) prob = < 0.001 lsd = 0.09).

At site 2, dry matter yield Figure 6.8 increased every season from 1 t/ha in 2009 to 5 t/ha in 2011, with a P application rate of 25 kg/ha. The soil at site 2 has a lower PBI than site 1 Table 6.2, PBI = 6.1 and shows a decrease in available soil P over the three seasons suggesting that P is not available to the plants as it is leached beyond the plant root zone. The plant P measurements for 2009 show that with more rainfall (43 days = 182 mm, 104 days = 411 mm, 125 days = 498 mm), the available soil P reduces, which is reflected in the concentration in plant shoots (see Figure 6.8).

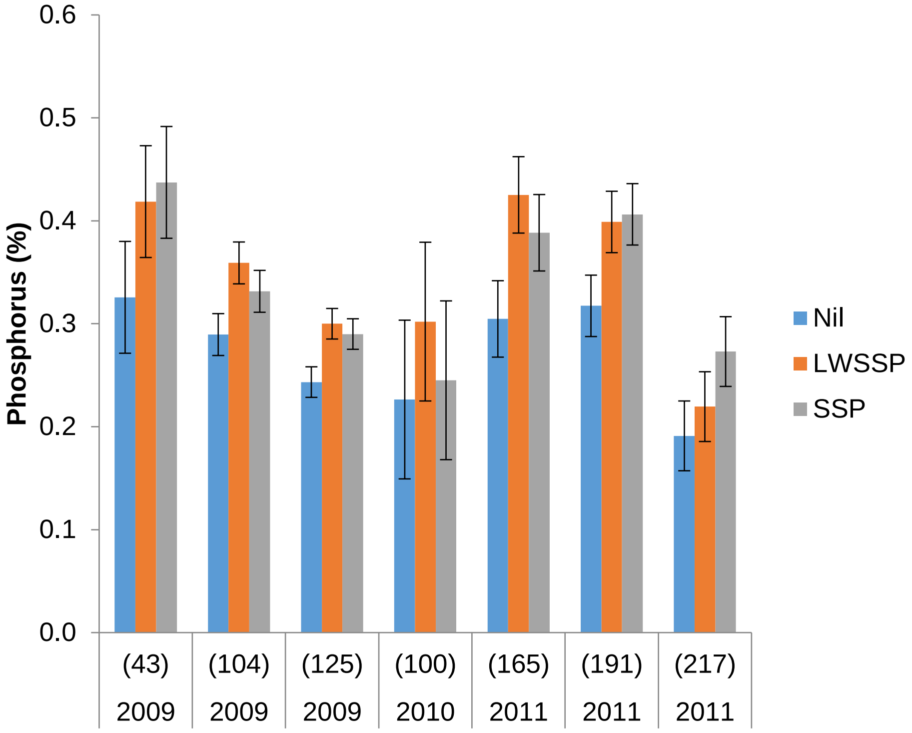


Figure 6.8 Field experiment site 2 phosphorus tissue analysis. Values in parentheses are days after application of phosphate fertiliser with the number below the year of sampling. The samples are concentrations of total phosphorus (%). Nil-P (Nil), low water-soluble superphosphate (LWSSP), single superphosphate (SSP) phosphate fertilisers were applied at 25 kg/ha of phosphorus. Error bars indicate the least significant difference for comparing phosphate forms between treatments (2009 (43), prob= 0.09 lsd = 0.11, (104), prob = 0.13 lsd = 0.04 (125), prob = 0.31 lsd = 0.03 2010 (100) prob = 0.048 lsd = 0.15 2011 (165), prob = 0.09 lsd = 0.07, (191), prob = 0.01 lsd = 0.06 (217), prob = 0.273 lsd = 0.03).

The 2011 season also show this trend of reducing tissue P with increased rainfall and available soil P. The difference between the 2009 season and the 2011 season is that much greater rainfall occurred during the early plant development in 2011, enabling greater plant growth and dry matter yield. These results show that using LWSSP causes no yield penalty on pasture production, compared to SSP.

The amount of growing season rainfall had a dramatic effect on the amount of dry matter yield during that season. The long-term average for the growing season (March–October) is 594 mm at Mandurah. Growing season rainfall for the 2009 and 2010 seasons was 517 mm and 432 mm respectively. Monthly rainfall in September and October was significantly reduced in both years. Consequently, the dry matter yield was limited by water deficiency. Growing season rainfall in 2011 was just below average with 575 mm.

The soil properties at each site are slightly different with site 1 having a greater ability to retain P but would likely require more moisture to allow plants to access it. In years where rainfall is less frequent, moisture would become limiting at both sites due to their soils being free draining and having low water-holding capacity.

6.3.2 Leaching column experiment

The leaching columns containing sand from field experiment 1 showed that applying P fertiliser undergoes significant leaching under simulated rainfall conditions. The majority of the MCP was rapidly leached within the first 300 mm of rainfall from both SSP and LWSSP (see Figure 6.9).

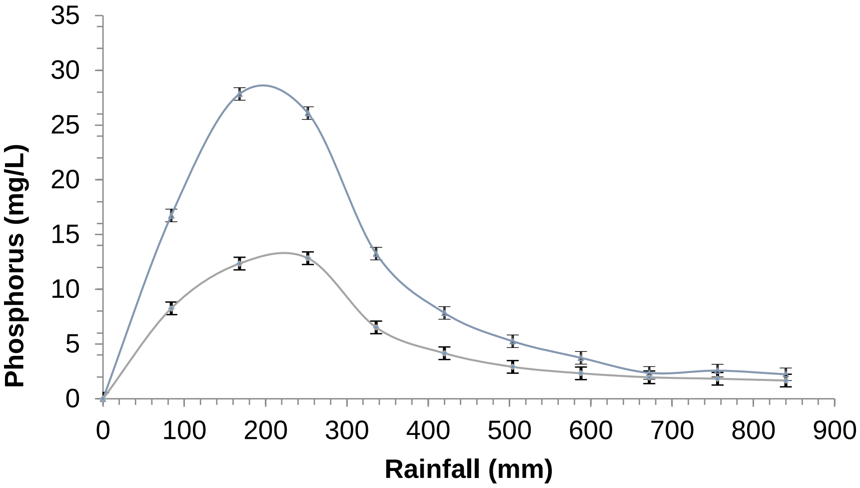


Figure 6.9 Rate of dissolution of phosphate fertiliser rate of dissolution applied to leaching columns containing sand. The concentration of phosphorus in solution after each 84 mm of rainfall for a total of 840 mm. □ single superphosphate (blue), Δ low water-soluble superphosphate (green). The least significant difference for comparing phosphate forms between treatments (lsd = 1.15).

Reducing the solubility of SSP by increasing the percentage of DCP (i.e. forming LWSSP) significantly reduces the concentration of water soluble P in the solution pool by almost 50% (see Figure 6.9). A total of 60 mg P/L leached from LWSSP compared to a total of 110 mg/L from SSP. This quantity of P leached means that the majority of the P applied from SSP is lost during the first half of the growing season where plant P requirements are high. Since the use of LWSSP fertiliser does not affect the optimum plant growth, substitution of SSP with LWSSP is preferable in this high rainfall and sandy soil conditions.

The loss of applied P through leaching follows the predicted solubility of each phosphate form and was significantly reduced with LWSSP compared to SSP over each sampling event because of the lower amount of MCP (see Table 6.3). The total cumulative rates at which each P fertiliser dissolves to MCP follows the trends indicated by the concentrations (see Figure 6.10).

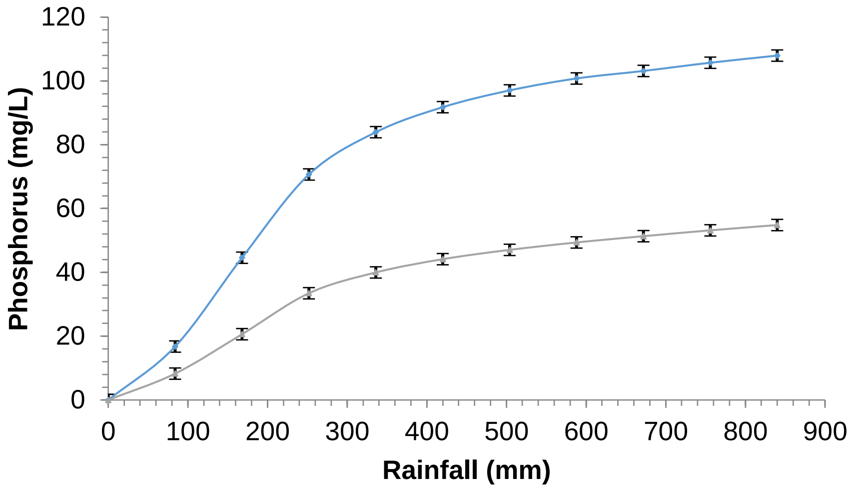


Figure 6.10 Cumulative rate of dissolution of phosphate fertiliser applied to leaching columns containing sand. The cumulative concentration of phosphorus in solution after each 84 mm of rainfall for a total of 840 mm. □ single superphosphate (blue) and Δ low water-soluble superphosphate (green). The least significant difference for comparing phosphate forms between treatments (lsd = 3.54).

The majority of P in MCP was leached during the first 300 mm of rainfall and DCP dissolves at a slower rate. These results are consistent with results outlined in (Chapter 4).

The amount of P leached during each of the growing seasons with rainfall greater than 300 mm would be minimal since the majority of P is leached within the first 300 mm. There is significantly less leaching of P with LWSSP compared to SSP ($p < 0.05$). This research provides evidence that increasing the proportion of DCP in P fertiliser in high leaching environments will significantly reduce P leaching, compared to high water-soluble P fertiliser, while maintaining pasture dry matter yield. The amount of P fertiliser required for optimum dry matter yield is well established, with several P fertiliser recommendation models developed from a large number of glasshouse and field experiments. These models are based on soil physiochemical properties (Colwell P, pH, PBI), and the plant requirements for P (see Figure 6.11). However, these current P fertiliser recommendation models often only account for the amount of P required for 95% of maximum plant growth and do not take into account the potential leaching of P from fertiliser use. The findings of this research can be used to improve current fertiliser models by determining the optimum ratio of MCP and DCP to significantly reduce P leaching and maximising plant growth as shown in Figure 6.11. This research value-adds to existing P models by introducing the concept of customising of P fertiliser to specific environmental conditions on SCP (see Figure 6.12).

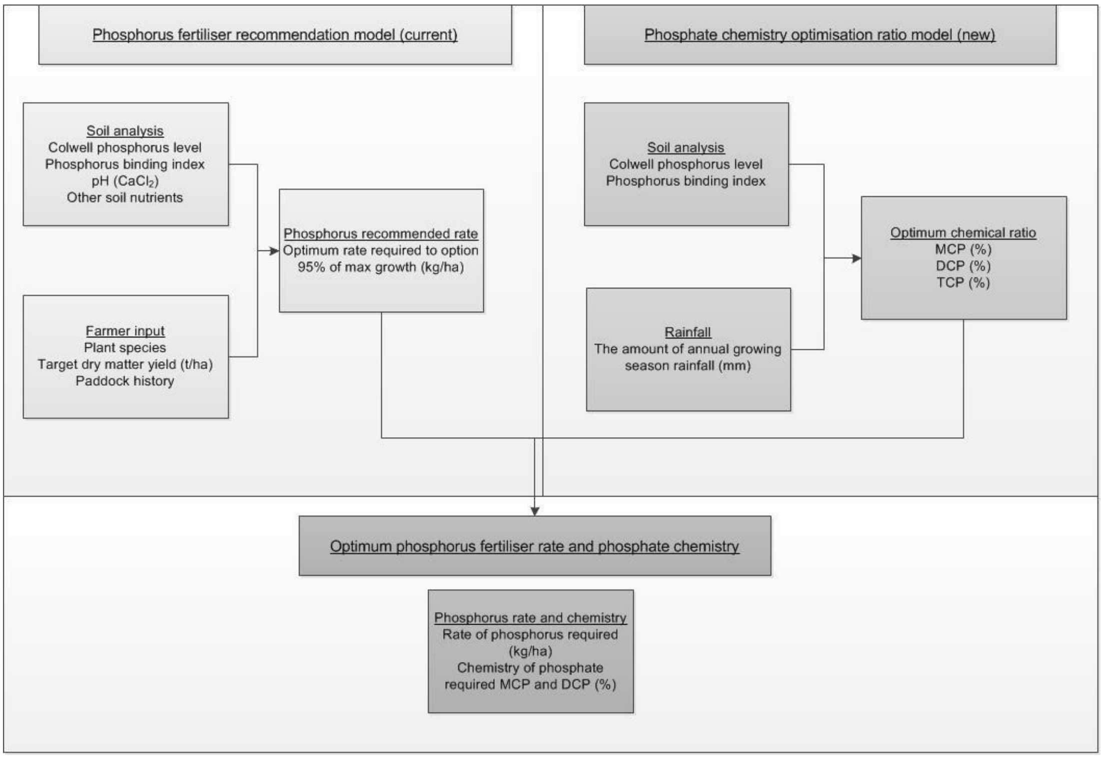
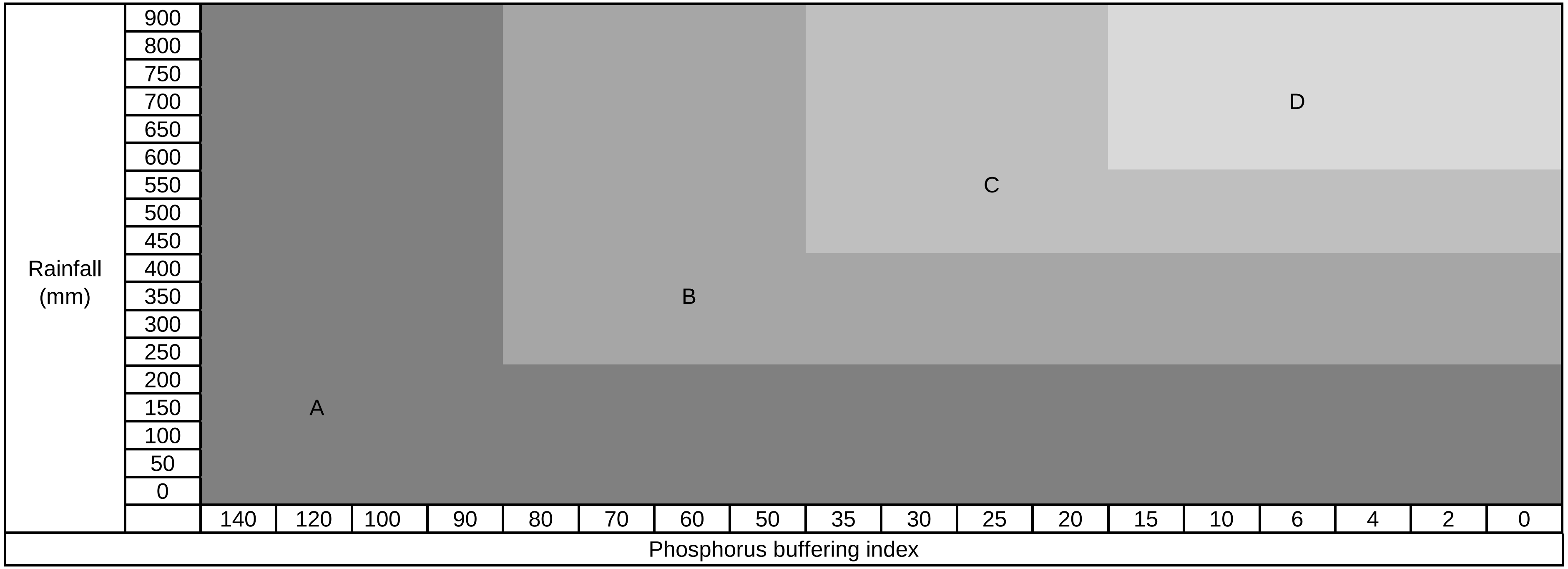


Figure 6.11 Proposed fertiliser solubility model. New integrated model for reducing phosphorus fertiliser leaching while maintaining optimum pasture growth on the SCP. The model integrates the current fertiliser recommended rate method with a new phosphorus optimising chemistry ratio model, to provide a recommend rate phosphorus rate (kg/ha) and optimum chemistry. Monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP). Tribasic calcium phosphate is considered an ineffective form for pasture production because it dissolves too slowly for plant growth, but it is a by-product of the manufacturing process and cannot be removed.



Band	MCP (%)	DCP (%)	TCP* (%)	Fertiliser ratio
A	86	9	5	SSP (100)
B	69	21	10	SSP (80): LWSSP (20)
C	52	33	15	SSP (60): LWSSP (40)
D	35	45	20	LWSSP (100)

Figure 6.12 Phosphate optimisation chemistry model. Values in parentheses are the percentage of each P fertiliser. This model uses the concept of manipulating the chemical ratio of monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP) within phosphate fertiliser to reduce phosphorus leaching and to maintain optimum pasture growth. Single superphosphate (SSP), low water-soluble superphosphate (LWSSP) The phosphorus buffering index was based on the scale outlined by Price (2006) with < 15 is extremely low, 15–35 is very very low, 36–70 is very low and 71–140 is very low. While this model is based on a limited dataset, it provides a guide for the reduction in phosphorous leaching and may not apply to all environmental conditions. *Tribasic calcium phosphate is considered an ineffective form for pasture production because it dissolves too slowly for plant growth, but it is a by-product of the manufacturing process and cannot be removed.

This model proposes that a significant reduction in leaching loss on soils with a PBI of below 120 can be obtained through determining the optimum fertiliser rate and then overlaying the new phosphate optimisation chemistry model (Chapter 5).

This new model has a basic structure with a sliding scale on the X and Y axis of a graph containing the relative amount of MCP and DCP required. The X axis is PBI (140–0), and the Y axis is rainfall (0–900 mm), and the basic output is determined by the intersection of these two variables. For example, the two field sites with PBI's outlined the optimum mixture would be LWSSP. This model is optimised for high rainfall sites in Western Australian, but it also is a good diagnostic tool for other locations in Australia. For example Table 6.4 shows the optimum chemistry mixture of phosphates for three soils with differing PBI and rainfalls.

Table 6.4 Examples of phosphate optimisation chemistry model.

Three examples of the ratio of monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP) within phosphorus fertiliser for reducing phosphorus leaching and maintaining optimum pasture growth.

Soil PBI	Rainfall (mm)	MCP (%)	DCP (%)	TCP (%)
9	800	35	45	20
16	300	69	21	10
123	900	86	9	5

6.4 Summary

Low water soluble superphosphate is manufactured from SSP fertiliser with MCP being replaced with DCP to ensure MCP is below 40% of the total phosphorus. There was no significant difference in plant dry matter yield or P uptake following the application of SSP or LWSSP fertiliser at comparable P rates. The analysis of three years of field experiment results indicated that plants could access adequate P regardless of the type of fertiliser (SSP or LWSSP). However, under simulated rainfall conditions of up to 840mm on a soil low in available P and low PBI (< 10), there was a significant decrease in leaching of applied P when LWSSP was compared to SSP. These results reinforced the results from previous Chapters (4 and 5) and indicate that increasing the amount of DCP allows an extended period for applied P to enter the solution pool from the active pool. Analysis of the soil (pre and post) from the field experiments also indicated that modifying the phosphate chemistry increased the amount of plant available P contained within the soil over three years of applications.

Leaching is considered when P has moved below the rhizosphere and becomes unavailable for the plants to access. As shown in Figure 6.10, the impact of DCP in the LWSSP fertiliser is from the different proportions of MCP (85% vs 40%) by DCP in the fertiliser. The DCP leaches more slowly and represents the difference between the two curves and clearly shows that DCP does not impact on MCP solubility and leaching. It can be concluded that DCP is beneficial to fertiliser manufacture and increasing the amount of DCP will decrease the amount of P that can be leached.

The amount of P fertiliser that is required to maximise dry matter yield is determined through P fertiliser recommendation models that use soil analysis and farmer input to determine the rate of application. The current limitations of these models is that they do not take into account the fertiliser solubility and rate of dissolution and size of the active P and solution P pools. Therefore P fertiliser applied with high concentrations of MCP (i.e. SSP) to soils with low sorption capacity would lead to leaching below the rhizosphere under higher rainfall conditions. The proposed model based on this research will allow farmers and consultants to determine the most optimum phosphate chemistry for any given soil type to reduce P leaching while maintaining dry matter yield for a range of situations based on the rainfall and a soil PBI. An option of combining fertilisers based on differing ratios of MCP and

DCP forms such as SSP and LWSSP will improve farming systems by reducing the amount of P leached without a reduction in pasture growth.

CHAPTER 7 GENERAL DISCUSSION

7.1 Introduction

The research of the thesis found that the difference in phosphate solubility created from customising the manufacture of single superphosphate fertilisers (SSP) can be used to create low water-soluble superphosphate (LWSSP) and reduce phosphorus (P) loss in pasture systems. On soils susceptible to leaching (i.e. SCP), this research verifies the impact of different fertiliser solubilities on plant dry matter yield, P uptake and P leaching in a range of experimental and field conditions. Figure 7.1 shows the order in which this research was undertaken and Chapter 6 includes the integration of the experimental results into a model.

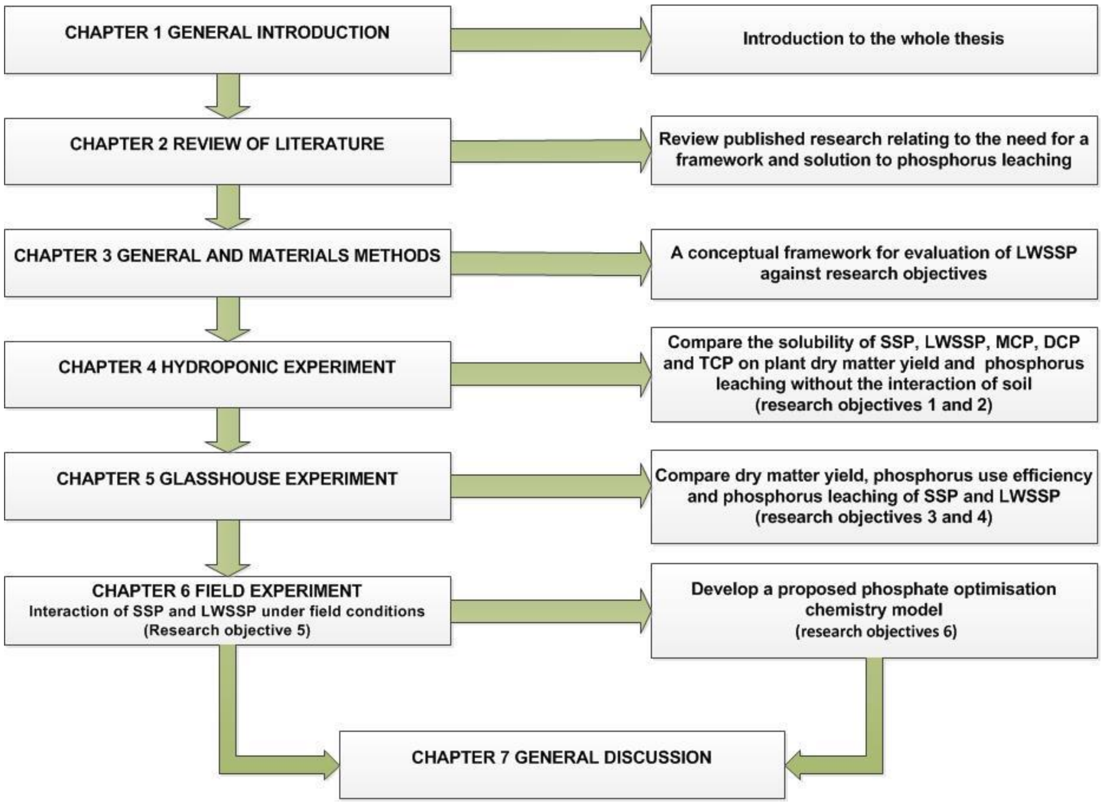


Figure 7.1 Conceptual framework of this thesis. Single superphosphate (SSP), low water-soluble superphosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP), tribasic calcium phosphate (TCP).

The development of the experimental model was via a step-wise process to explain the interaction of phosphate solubility, plant and soil in leaching, glasshouse and field experiments over 3 years as a pasture production system. It is important to recognise that this research was started in 2009 when the Fertiliser plan was to be implemented and a fertiliser suitable for the SCP was not available. This research has led to the commercialisation of LWSSP as a “Super SR” with fertiliser production since 2010 being well over 100,000 tonnes. It was the research conducted as part of this PhD that verified the properties of this new fertiliser product in a pasture system.

7.2 To compare the P solubility and leaching of LWSSP and SSP fertilisers and their chemical components for pasture production in hydroponic no-soil conditions

This research found that the dissolution of various calcium phosphate fertilisers is governed by their relative solubility and follows the principles outlined by (Shen *et al.* 2011). The rate that a fertiliser dissolves (i.e. SSP, LWSSP) without soil depends on the components of that fertiliser (Gilkes and Lim-Nunez 1980). Each component of the SSP and LWSSP fertilisers Table 4.1 has different rates of solubility and once P is in solution and has become saturated, an equilibrium is reached (Huffman *et al.* 1957). This equilibrated P solution will be maintained unless P is removed by the plant, in which more P will dissolve until the solution becomes saturated again (Richardson *et al.* 2009a).

The hydroponic research demonstrates that plant dry matter yield matches the chemical reaction concept of fertiliser solubility where the MCP dissolves quickly into solution and significantly increases yield as outlined by (Kotz *et al.* 2003). For the components of P fertilisers as explained by Edmeades (2000) with MCP dissolving very rapidly to reach saturation, while DCP which is less soluble and will reach the same saturation process in water over a longer period. For TCP which is very insoluble, dissolves very slowly with only a minimal amount of P available in solution for access by the plant (Tebman *et al.* 1958). Tribasic calcium phosphate is considered ineffective as a plant fertiliser, but it is present in fertiliser as a by-product of the fertiliser manufacturing process and cannot be removed (Bolland *et al.* 1997; Darlow 2009).

The leaching column research using perlite as a soil substitute (i.e. without interaction of soil or plant properties that can influence the rate and amount of P leaching) showed that different rates of leaching and correlated to phosphate solubility. As water is added to the top of the column, the MCP dissolves rapidly in contact with water, and as the water leaches down the column, this dissolved P is available to the plant when present in the rhizosphere.

This research was unique in the investigation and validation of different phosphate forms and chemistry of SSP in regards to solubility, plant dry matter yield and P uptake. While the chemistry of SSP is well understood, the chemical manipulation of this chemistry to reduce leaching while maintaining plant dry matter yield and P uptake was not. This research has validated the solubility of SSP, LWSSP and its component phosphates MCP, DCP and TCP. These results can now be used to create a new generation of P pasture fertilisers with new phosphate chemistry to match pasture plant requirements for P and environmental rainfall in a way that has not been implemented previously.

7.3 To compare P solubility, leaching and pasture production characteristics for LWSSP and SSP on three soil types soil under controlled glasshouse conditions

The amount of P available to the plant is defined by, its root area, the amount of P in solution, the ability to adsorb P, and the ability of the soil to retain P (Niu *et al.* 2012). This research showed differences in fertiliser components (MCP, DCP and TCP) for different soil types. The concept developed from this research is that the percentage of MCP and DCP can be varied to ensure the amount of P in solution does not limit plant dry matter yield while reducing the amount of P lost to leaching. Since early plant growth roots have a limited surface area from which to obtain P from solution, monobasic calcium phosphate rapidly dissolves P into solution for the plant to access, but access time can be reduced if the soil has a low ability to retain P in solution and subsequent rainfall events leach P below the plant’s root zone (Rajan 1987). Dibasic calcium phosphate is less soluble and enters solution at a slower rate than MCP and this reduced solubility increases the amount of time that plants can obtain P from solution before it is leached after rainfall. Clover and ryegrass have different requirements for P and different abilities to obtain P from solution, with ryegrass having a more fibrous root system and hence a greater surface area to adsorb P. Even with different root systems, clover and ryegrass requirement for P depends on the growth stage and root development and the amount of P that a plant can adsorb is affected by the amount of P in solution.

This research was unique in the investigation and validation of LWSSP phosphate chemistry to reduce P leaching, to maintain pasture dry matter yield and P uptake on three soil types with a range of PBI. The phosphate chemistry (DCP to MCP ratio) of LWSSP is unique and has never been investigated previously to reduce the environmental damage from P leaching. The chemical phosphate of LWSSP has been designed for extreme leaching conditions but can be manipulated based on this research to a range of soil conditions for pasture production. These research results have shown that soils with a PBI of > 120 are not susceptible to P loss to leaching and regardless of rainfall should be disregarded from future research into this subject. The result of this research also indicates that phosphate chemistry should take into account different soils type and rainfall conditions. This method of matching the plant's requirement for P, the soils ability to retain P, and rainfall is a new novel method for the applications of P fertilisers.

7.4 To compare LWSSP and SSP interactions on pasture growth by measurement dry matter yield, P plant tissue percentage and soil P levels in field conditions

This research demonstrated that with increased demand for P (i.e. by the plants from livestock feeding) in field experiments LWSSP had no less significant effect of plant dry matter yield than SSP. Pasture production systems are often established for the maximum food on offer for livestocks to be converted into meat, milk or wool. Phosphorus is required for early plant growth as well as for replacing plant tissue that is removed by livestocks. The removal of plant shoots increases the requirement for P which is taken up from solution by the plant roots. The amount of P which a plant can access in the field is determined by the rate at which P is dissolved into solution and the soil’s ability to retain P in solution. These factors create a P solution pool within the soil that increases in size as the soil’s ability to retain P increases. If the amount of P in solution is less than the plant requires then dry matter yield will be reduced, but if there is an excess of P, then P will be leached (see Figure 6.9). The plant requirements and access to the P solution pool will determine how much and at what rate P is removed from the solution pool Figure 7.2 demonstrates this P pool concept with three different tanks based on the soils ability to store P. Single superphosphate with a high percentage of MCP increases the rate that the tanks will fill. If the tanks fill too rapidly the excess will be lost. Reducing the solubility of the fertiliser by increasing the percentage of DCP reduces the rate at which the P solution pool is filled and also increases the amount of time that plants can access the P before it is lost to leaching.

This research was unique in demonstrating that phosphate chemistry modification is a key contribution to better plant growth. The novelty of the new LWSSP phosphate chemistry with a DCP level of 35% has been proven to maintain pasture dry matter yield and P uptake in multi-environment locations. From the results of experiments outlined in Chapters 4 and 5, farmers have already begun to implement these findings. This new approach will allow farmers to maintain pasture production systems, reduce environmental damage and utilise existing equipment. As the new LWSSP is manufactured using the same infrastructure and base products, the cost to the farmer is the same per P kg/ha applied as SSP. All these factors suggest that this novel approach to the reduction of P leaching could be implemented globally regardless of the soil type, rainfall or location.

7.5 Develop a concept that models how LWSSP can fit into the agricultural system based on rainfall and P buffering index

This research concept shows that the optimum situation is to match the size of the P solution pool to the chemistry of the fertiliser so that the pool always remains full but not overflowing (i.e. leaching). Fertiliser will always require a minimum amount of MCP to fill the pool rapidly with the amount of DCP determined by the size of the pool and the amount of rainfall to dissolve the P into solution.

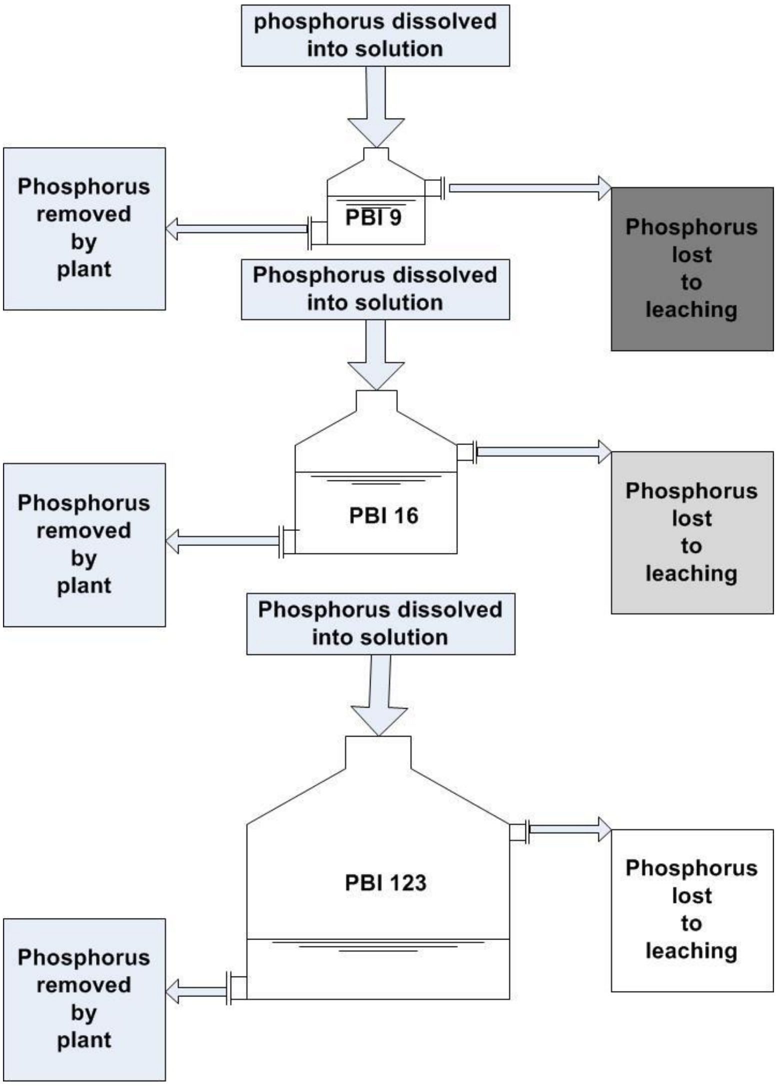


Figure 7.2 The phosphorus solution pool. As the phosphorus buffering index (PBI) increases, so does the relative amount of soluble phosphorus that is stored within the soil before it is unable to store anymore and it is lost to leaching.

The balance between what is available to a plant and the plant's requirements for P determine how well and at what rate the plant will grow. The solubility of LWSSP and SSP determines the concentration and rate that the P dissolves into solution and the amount that enters the P solution pool at any given time (Malik *et al.* 2012). Single superphosphate dissolves into solution and enters and exits the P solution pool very rapidly. Low water-soluble superphosphate with its lower solubility slows down the amount of P that enters the P solution pool and increases the amount of time that plants can access the pool before the P exits and is lost to leaching. A less soluble fertiliser will require more moisture over the season to dissolve the equivalent amount of P into the solution pool.

The gap in knowledge that is addressed by this research is in determining how to apply this information to a pasture production system. The data from this research shows a predictable response for MCP and DCP for pasture production but not TCP. The reason for this may be due to the MCP, and DCP is more soluble typically with pasture production rainfalls of 400–900 mm compared to TCP. The amount of rainfall affects the amount of P in solution in the plant root zone and the amount of rainfall required to dissolve MCP, DCP, TCP, LWSSP and SSP into solution.

This research demonstrated that the fertiliser and the pasture species significantly affect the amount of P leaching through the soil. The difference in leaching of the fertiliser is a function of their solubility, and the differences in P leaching from the pasture species is a function of their roots increasing the permeability of the soil. The plants also extract P from the soil for dry matter production, which reduces the amount of P that is leached. Applying LWSSP significantly reduced P leaching, compared to SSP on the light and medium soil types. As the PBI increases, the amount of P leached significantly reduces, regardless of fertiliser type or plant species. These plant dry matter yield results confirm that LWSSP is a viable replacement for SSP for pasture production in these conditions. In summary, the research in this thesis is novel in that it found that the differences in solubility created from customising fertiliser manufacturing of SSP can be used to reduce phosphorus loss in pasture systems in high rainfall regions of Western Australia.

7.6 Future direction and research

This research has outlined that modifying the chemistry of SSP to LWSSP is a viable, practical solution for maintaining pasture dry matter yield and significantly reducing P leaching. The phosphate optimisation chemistry model developed from this research outlines a new method for customising of MCP and DCP within fertilisers to reduce P leaching based on PBI and rainfall.

It is recommended that further research and development be conducted to increase the accuracy of this model, with a greater number of different ratios of MCP and DCP over a range of soil types with a PBI between 1 and 120. It is suggested that 10–15 soils across a range of soils based on PBI be selected with low Colwell P levels that are based on current P fertiliser recommendation models such as better fertiliser decisions and CSBP Limited Nulogic software (Dowling 2015; Neuhaus 2015). For each soil type, the four (A, B, C and D) mixtures of MCP and DCP be applied (see Figure 6.12). Since the manufacturing properties of LWSSP will not allow the amount of DCP to increase (above 35%) as the granular strength is reduced and it will not be able to be applied using current farmer machinery. However, the amount of DCP can be reduced to current SSP levels (i.e. 8%) and changed to any level in between. This range of DCP should be investigated in conjunction with rainfall to refine the model. The recommended methodology for this investigation would be equivalent to the glasshouse experiment (Chapter 5) and vary the soil types and rainfall amount.

The research has identified that TCP is not a plant available form of P and it is recommended that pasture fertiliser is manufactured without it. The process could be conducted by combining the pure forms of MCP and DCP into a fertiliser granule. However, it is yet to be seen if it will be cost effective method as SSP produced from rock phosphate is still relatively cheap.

During this research, it has been noted that SSP also contains sulphur that is a critical macronutrient for plant production. The sulphur is present in a highly water soluble form, and while the manipulation of SSP phosphate chemistry has reduced P loss, sulphur can be leached. This loss will limit pasture production and it is recommended that research is conducted to reduce sulphur leaching with the introduction of elemental sulphur into SSP as a starting point. The research within this thesis has proven the concept of manipulating phosphate chemistry and the researcher hopes that future research continues and improves on the novel technology and ideas contained within.

CHAPTER 8 REFERENCES

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CHAPTER 9 APPENDIX

9.2 Review of literature

9.2.1 Table 9.1 Australia soil classification system.

(Burkitt *et al.* 2002; Isbell 2016)

Name	Texture	Description
Anthroposols		Soils resulting from human activities which have led to a profound modification, truncation or burial of the original soil horizons, or the creation of new soil parent materials by a variety of mechanical means. Where burial of a pre-existing soil is involved, the anthropic materials must be 0.3 m or more thick. Pedogenic features may be the result of in situ processes (usually the minimal development of an A1 horizon, sometimes the stronger development of typical soil horizons) or the result of pedogenic processes before modification or placement (i.e. the presence of identifiable pre-existing soil material).
Calcarosols		Soils that are calcareous throughout the solum – or calcareous at least directly below the A1 or Ap horizon, or a depth of 0.2 m (whichever is shallower). Carbonate accumulations must be judged to be pedogenic1 (either current or relict), and the soils do not have clear or abrupt textural B horizons. Hydrosols, Organosols and Vertosols are excluded.
Chromosols	Loamy sand	Soils other than Hydrosols with a clear or abrupt textural B horizon and in which the major part of the upper 0.2 m of the B2 horizon (or the major part of the entire B2 horizon if it is less than 0.2 m thick) is not sodic and not strongly acid. Soils with strongly sub-plastic upper B2 horizons are also included even if they are sodic.
Dermosols	Silty clay loam	Have B2 horizons with structure more developed than weak1 throughout the major part of the horizon, and Do not have clear or abrupt textural B horizons.
Ferrosols	Clay	Have B2 horizons in which the major part has a free iron oxide free iron oxide1 content greater than 5% Fe in the fine earth fraction (< 2 mm), and Do not have clear or abrupt textural B horizons or a B2 horizon in which at least 0.3 m has vertic properties.
Hydrosols	Clay loam	Soils other than Organosols, Podosols and Vertosols in which the greater part of the profile is saturated for at least 2–3 months in most years.
Kandosols	Silty clay	B2 horizons in which the major part is massive or has only a weak grade of the structure. A maximum clay content in some part of the B2 horizon which exceeds 15% (i.e. heavy sandy loam, SL+). Do not have a tenic B horizon. Do not have clear or abrupt textural B horizons. Are not calcareous throughout the solum, or below the A1 or Ap horizon or to a depth of

Name	Texture	Description
		0.2 m if the A1 horizon is only weakly developed.
Kurosols	Silty loam	Soils other than Hydrosols with a clear or abrupt textural B horizon and in which the major part of the upper 0.2 m of the B2 horizon (or the major part of the entire B2 horizon if it is less than 0.2 m thick) is strongly acid.
Organosols		Have more than 0.4 m of organic materials within the upper 0.8 m. The required thickness may either extend down from the surface or be taken cumulatively within the upper 0.8 m. or Have organic materials extending from the surface to a minimum depth of 0.1 m, these either directly overlie rock or other hard layers, partially weathered or decomposed rock or saprolite, or overlie fragmental material such as gravel, cobbles or stones in which the interstices are filled or partially filled with organic material. In some soils there may be layers of humose and/or melacic horizon material underlying the organic materials and overlying the substrate.
Podosols	Sand	Soils which possess either a Bs horizon (visible dominance of iron compounds), a Bhs horizon (organic-aluminium and iron compounds), or a Bh horizon (organic-aluminium compounds). These horizons may occur singly in a profile or in combination (see Podosol diagnostic horizons).
Rudosols		Soil with negligible (rudimentary) pedologic organisation apart from (a) minimal development of an Al horizon or (b) the presence of less than 10% of B horizon material (including pedogenic carbonate) in fissures in the parent rock or saprolite. The soils are apedal or only weakly structured in the A1 horizon and show no pedological colour changes apart from the darkening of an A1 horizon. There is little or no texture or colour change with depth unless stratified or buried soils are present.
Sodosols	Sandy loam	Soils with a clear or abrupt textural B horizon and in which the major part of the upper 0.2 m of the B2 horizon (or the major part of the entire B2 horizon if it is less than 0.2 m thick) is sodic and not strongly acid. Hydrosols and soils with strongly sub-plastic upper B2 horizons are excluded.
Tenosols	Sandy clay loam	A peaty horizon. A humose, melacic or melanic horizon, or conspicuously bleached A2 horizon, which overlies a calcrete pan, hard unweathered rock or other hard materials, or partially weathered or decomposed rock or saprolite, or unconsolidated mineral materials. A horizons which meet all the conditions for a peaty, humose, melacic or melanic horizon except the depth requirement, and directly overlie a calcrete pan, hard unweathered rock or other hard materials, or partially weathered or decomposed rock or saprolite, or unconsolidated mineral materials. A1 horizons which have more than a weak development of structure and directly overlie a calcrete pan, hard

Name	Texture	Description
		unweathered rock or other hard materials, or partially weathered or decomposed rock or saprolite, or unconsolidated mineral materials. An A2 horizon which overlies a calcrete pan, hard unweathered rock or other hard materials, or partially weathered or decomposed rock or saprolite, or unconsolidated mineral materials. Either a tenic B horizon, or a B2 horizon with 15% clay (SL) or less1 , or a transitional horizon (C/B) occurring in fissures in the parent rock or saprolite which contains between 10 and 50% of B horizon material (including pedogenic carbonate). A ferric or bauxitic horizon > 0.2 m thick. A calcareous horizon > 0.2 m thick.
Vertosols	Loam	A clay field texture or 35% or more clay throughout the solum except for thin, surface crusty horizons 0.03 m or less thick and. When dry, open cracks occur at some time in most years1. These are at least 5 mm wide and extend upward to the surface or to the base of any plough layer, peaty horizon, self-mulching horizon, or thin, surface crusty horizon, and Slickensides and/or lenticular peds occur at some depth in the solum.

9.2.2 Swan Coastal Plain soil-landscape systems (soil classifications)

(Gool *et al.* 2005)

Quindalup South System
Coastal dunes, of the Swan Coastal Plain, with calcareous deep sands and yellow sands. Coastal scrub.

Spearwood System
Sand dunes and plains. Yellow deep sands, pale deep sands and yellow/brown shallow sands.

Bassendean System
Swan Coastal Plain from Busselton to Jurien. Sand dunes and sandplains with pale deep sand, semi-wet and wet soil. Banksia-paperbark woodlands and mixed heaths.

Moore River System
Alluvial flats: Swan Coastal Plain west of Gingin, wet soil, semi-wet soil, pale and yellow deep sands, Woodlands and heaths.

Yanga System
Poorly drained plain with pale sands and deep sandy duplex, wet, semi-wet and saline wet soils. Banksia-pricklybark-marri-swamp sheoak-paperbark woodlands.

Forrestfield System
Undulating foot slopes of the Darling and Whicher Scarps. Duplex sandy gravels, pale deep sands and grey deep sandy duplexes. Woodland of *E. marginata*, calophylla and wandoo and some *B. grandis*.

Vasse System
Poorly drained estuarine flats, of the Swan Coastal Plain. Tidal flat soil, saline wet soil and pale deep sand. Samphire, sedges and paper bark woodland.

Abba System
Poorly drained flats, on the southern Swan Coastal Plain. Grey deep sandy duplex and wet soil. Jarrah-marri-paperbark woodland.

Willyabrup Valleys System
Granitic valleys, in the Leeuwin Zone. Loamy gravel, sandy gravel and loamy earth. Jarrah-marri-karri forest.

Cowaramup Uplands System
Lateritic plateau, in the Leeuwin Zone. Sandy gravel, loamy gravel and grey sandy duplex. Jarrah-marri forest.

Gracetown Ridge System
Limestone ridge, in the coastal edge of the Leeuwin Zone. Yellow deep sand and red deep sand. Coastal scrub, peppermint woodland and jarrah-marri-karri forest.

9.3 General methods and materials

9.3.1 Correspondents from Dr Stephen Loss (26 May 2015)

Rowan

I now recall reviewing the lab methods when I was there. I remember there were two set of methods – a brief summary of each test for external use, and a detailed one only for internal use. There will be no problem in using the external summaries.

Cheers

Dr Stephen Loss

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9.3.2 Hydroponics experimental notes and attachments

9.3.2.1 Hydroponics

Table 9.2 Hydroponic full experimental design (2014).

Trt	Tank	Species	Fertiliser	P kg/ha
Run 1				
1	1	Clover	Nil-P	0
2	1	Ryegrass	Nil-P	0
5	2	Clover	Low water-soluble superphosphate	25
6	2	Ryegrass	Low water-soluble superphosphate	25
3	3	Clover	Singe superphosphate	25
4	3	Ryegrass	Singe superphosphate	25
Run 2				
7	1	Clover	Monobasic calcium phosphate	25
8	1	Ryegrass	Monobasic calcium phosphate	25
9	2	Clover	Dibasic calcium phosphate	25
10	2	Ryegrass	Dibasic calcium phosphate	25
11	3	Clover	Tribasic calcium phosphate	25
12	3	Ryegrass	Tribasic calcium phosphate	25
Run 3				
3	1	Clover	Singe superphosphate	25
4	1	Ryegrass	Singe superphosphate	25
7	2	Clover	Monobasic calcium phosphate	25
8	2	Ryegrass	Monobasic calcium phosphate	25
9	3	Clover	Dibasic calcium phosphate	25
10	3	Ryegrass	Dibasic calcium phosphate	25
Run 4				
5	1	Clover	Low water-soluble superphosphate	25
6	1	Ryegrass	Low water-soluble superphosphate	25
11	2	Clover	Tribasic calcium phosphate	25
12	2	Ryegrass	Tribasic calcium phosphate	25
1	1	Clover	Nil-P	0
2	1	Ryegrass	Nil-P	0

Trt	Tank	Species	Fertiliser	P kg/ha
Run 5				
9	1	Clover	Dibasic calcium phosphate	25
10	1	Ryegrass	Dibasic calcium phosphate	25
3	2	Clover	Singe superphosphate	25
4	2	Ryegrass	Singe superphosphate	25
5	3	Clover	Low water-soluble superphosphate	25
6	3	Ryegrass	Low water-soluble superphosphate	25
Run 6				
11	1	Clover	Tribasic calcium phosphate	25
12	1	Ryegrass	Tribasic calcium phosphate	25
1	2	Clover	Nil-P	0
2	2	Ryegrass	Nil-P	0
7	3	Clover	Monobasic calcium phosphate	25
8	3	Ryegrass	Monobasic calcium phosphate	25

Table 9.3 Hydroponics plant position design (2014).

Pot no.	Tank 1	Tank 2	Tank 3
Run 1			
1	Ryegrass	Ryegrass	Clover
2	Clover	Clover	Ryegrass
3	Ryegrass	Ryegrass	Ryegrass
4	Clover	Ryegrass	Clover
5	Ryegrass	Clover	Ryegrass
6	Clover	Clover	Clover
Run 2			
1	Ryegrass	Clover	Ryegrass
2	Clover	Ryegrass	Clover
3	Ryegrass	Clover	Ryegrass
4	Clover	Ryegrass	Ryegrass
5	Ryegrass	Clover	Clover
6	Clover	Ryegrass	Clover
Run 3			
1	Ryegrass	Clover	Ryegrass
2	Clover	Ryegrass	Clover
3	Clover	Clover	Clover
4	Ryegrass	Ryegrass	Clover
5	Clover	Ryegrass	Ryegrass
6	Ryegrass	Clover	Ryegrass

Pot no.	Tank 1	Tank 2	Tank 3
Run 4			
1	Clover	Ryegrass	Clover
2	Ryegrass	Clover	Ryegrass
3	Ryegrass	Clover	Ryegrass
4	Clover	Ryegrass	Clover
5	Clover	Ryegrass	Clover
6	Ryegrass	Clover	Ryegrass
Run 5			
1	Ryegrass	Ryegrass	Clover
2	Clover	Ryegrass	Clover
3	Ryegrass	Ryegrass	Clover
4	Clover	Clover	Ryegrass
5	Ryegrass	Clover	Ryegrass
6	Clover	Clover	Ryegrass
Run 6			
1	Ryegrass	Clover	Ryegrass
2	Clover	Ryegrass	Ryegrass
3	Ryegrass	Clover	Clover
4	Clover	Clover	Clover
5	Clover	Ryegrass	Clover
6	Ryegrass	Ryegrass	Ryegrass

Table 9.4 Hydroponics experiment visual observations and actions (2014). Single superphosphate (SSP), low water-soluble superphosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP).

Date	Actions	Run
7 June	Talked to Sandro and he has given me the following information about the nutrient solution mixture that he has made for the experiment: Apply 3 mL/L of A and B 40 L in the tanks, so the starting mixture will be: 120 mL of both A and B target EC between 1.4–2.0, Target pH 5.8–6.4 (Rowan Maddern).	2–1
16 June	Experiment restarted and potted up run 1. Added 120 mL of A and 120 mL of B to the tanks. EC was about 1.4 and pH was about 4 so added 4 mL/tank of pH up to each tank. Plant density increased to 20 plants per pot to increase demineralised water for analysis. Photos were taken and samples from all tanks as well as the A and B part of the nutrient solution mixture (Rowan Maddern and Dean Diepeveen).	2–1 Start
20 June	Plants look good and samples taken from all 3 tanks. EC are about 1.8 and pH is up 8.0. Added 2 litres demineralised water to each tank. Talked to Deb and Brad and we have worked out that adding sulphurise acid and not phosphoric acid as within the pH down. Dropped off 180 L of demineralised water off. Photos taken (Rowan Maddern).	2–1 Week 1
26 June	Experiment check EC and pH and EC was about 1.5 and pH was about 8. Added 0.5 mL/tank hydrochloric acid to each tank as recommended by Brad. Check the levels again and the pH had dropped to 7.0.Water samples indicated that the nil P tank has some P in the water. Tank 3 SSP looks the best. Photos taken (Rowan Maddern).	2–1 Week 2
7 July	Harvested Run 1 and plants looked a lot better. Tank 1 still looked good with nil-P applied and for some reason that tank always looks good. Looks to be a plant weight response with SSP tank 3 wet weights greater than LWSSP wet weights tank 2. Rest set the tanks for the start of tank 2 and took water samples from the end of the last run and the start of this run. Photos taken (Rowan Maddern and Dean Diepeveen).	2–1 Harvest 2–2 Start
10 July	DMY water dropped off and EC and pH checked. pH was a little high so added 0.5 mL/tank acid. Plants look better and have grown over the last 3 days but ryegrass still looks a bit yellow. Photos taken (Rowan Maddern).	2–2 Checked
15 July	Water samples taken from all tanks, EC and pH are both in range. All pot growing well, not much too visual yet (Rowan Maddern).	2–2 Water samples Checked

Date	Actions	Run
21 July	Water samples taken from all tanks, EC and pH checked. pH was a little bit low so 1 mL/tank added to all tanks. 2 L of DM water added to each tank. All three tanks are growing very well, most growth to date. Not much visually. Photos were taken (Rowan Maddern).	2–2 Water samples Checked
28 July	Run 2 harvested with production, with the greatest being about 25 grams of wet matter weight. Water analysis indicated that tank 1 and tank 2 fertiliser may have been switched and will have to check the next run. Reset the tanks for run 3. Water samples were taken from the end of run 2 and the start of run 3. Photos were taken (Rowan Maddern and Dean Diepeveen).	2–2 Harvested 2–3 Started
4 Aug.	Water samples taken from all tanks and pH/EC checked. All tanks growing well but no responses yet as plants are still small. Photos were taken (Rowan Maddern).	2–3 Water samples Checked
11 Aug.	Water samples were taken and photos, looks like the order of best growth is MCP, DCP and then SSP. pH and EC both within range (Rowan Maddern).	2–3 Water samples Checked
18 Aug.	Run 3 harvested and wet weights look constant with increased growth as a function of increased solubility. Water samples taken from the end and start of both runs. Run 4 started. Photos were taken (Rowan Maddern and Dean Diepeveen).	2–3 Harvested 2–4 Started Water samples
26 Aug.	Water samples were taken, and the pH/EC checked, pH was high so 0.5 mL/tank acid added. Best pot is pot 1 then 2 and 3 Nil looks like it's dropping off. Photos were taken (Rowan Maddern).	2–4 Water samples checked
28 Aug.	Photos taken, tanks look good. Tank 3 was in 24 hours as it was plugged into the air stone board. Changed it over to fix it. Nil-P tank dropping off and LWSSP looks better than Tri (Rowan Maddern).	2–4 Checked
1 Sep.	Photos were taken and all tanks look good. Water samples were taken and 2 litres per tank demineralised water added. EC and pH both within range (Rowan Maddern).	2–4 Water samples Checked
5 Sep.	Photos taken of all tanks. Thinned the pots to 20 plants for run 5. Checked the pH and EC, pH was a little bit high 7.5 so added 0.5 mL/tank of acid to all tanks. Nil-P tank looking very poor as would be expected (Rowan Maddern).	2–4 Checked
8 Sep.	Run 4 harvested and run 5 started. Photos were taken and it looks like nil-P is very poor with only about 1.8 g per pot of both ryegrass and clover. Water samples were taken from the end of run 4 and the start of run 5 (Rowan Maddern, Brad Smith).	2–4 Harvested 2–5 Started Water samples
9 Sep.	Photos were taken, and pH and EC checked. pH was a bit high, so 1 mL/tank acid added (Rowan Maddern).	2–5 Checked
15 Sep.	Photos and water samples taken from all three tanks. pH was a little bit high, so 0.5 mL/tank acid added. Best	2–5 Checked

Date	Actions	Run
	growth was SSP, then LWSSP and DCP (Rowan Maddern).	Water samples
18 Sep.	Photos were taken, and EC/pH checked. pH on tanks 2 and 3 was low so added 1 mL/tank pH up to each. Everything else looks good with good plant growth (Rowan Maddern).	2–5 Checked
22 Sep.	Photos were taken, and the last load of demineralised water dropped off for run 6. EC and pH are checked and both ok. Added 2 L of demineralised water per tank and water samples taken (Rowan Maddern).	2–5 Checked Water samples
29 Sep.	Run 5 harvested and start of run 6. Photos were taken and look to good growth response to all treatments. Water samples taken from the end of run 5 and start of run 6. Set up run 6 (Rowan Maddern and Deb Pritchard).	2–5 Harvested 2–6 Started Water samples
6 Oct.	Experiment checked, and water samples were taken. Tank 2 nil-P has reduced growth and photos taken (Rowan Maddern and Dean Diepeveen).	2–6 Water samples Checked
13 Oct.	Experiment checked and water samples taken from all tanks. 2 litres of demineralised water added (Dean Diepeveen).	2–6 Water samples Checked
14 Oct.	Experiment checked, and water samples were taken. Photos were taken, and growth order was tank 3 MCP, tank 1 TCP and tank 2 nil-P (Rowan Maddern and Dean Diepeveen).	2–6 Checked
16 Oct.	Experiment checked, and photos were taken. Water level looks a little low in the tanks, and the plant looks a little burnt from the 35-degree day on the 15 Oct (Rowan Maddern and Brad Smith).	2–6 Checked
20 Oct.	Run 6 harvested and water samples taken. Responses were following solubility with MCP best, TCP and then nil-P. Photos were taken. End of the experiment (Rowan Maddern and Dean Diepeveen).	2–6 Harvested Water samples

9.3.2.2 Leaching column

Table 9.5 Leaching column full experimental design (2014). Single superphosphate (SSP), low water-soluble superphosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP).

Column no.	Trt	Bench	Row	Col	Applied	Medium	Form	P %
1	7	1	1	1	SSP	Perlite	Sieved	9.1
2	9	1	1	1	LWSSP	Light sand	Sieved	8.3
3	5	1	1	1	DCP	Perlite	Sieved	18.09
4	-	1	1	1	LWSSP	Light sand	Sieved	8.3
5	2	1	1	1	SSP	Perlite	Granular	9.1
6	6	1	1	1	TCP	Perlite	Sieved	15.89
7	1	1	1	1	Nil-P	Perlite	-	0
8	2	2	2	1	SSP	Perlite	Granular	9.1
9	1	2	2	1	Nil-P	Perlite	-	0
10	4	2	2	1	MCP	Perlite	Sieved	26.16
11	6	2	2	1	TCP	Perlite	Sieved	15.89
12	9	2	2	1	LWSSP	Light sand	Sieved	8.3
13	3	2	2	1	LWSSP	Perlite	Granular	8.3
14	8	2	2	2	LWSSP	Perlite	Sieved	8.3
15	3	3	1	2	LWSSP	Perlite	Granular	8.3
16	4	3	1	2	MCP	Perlite	Sieved	26.16
17	8	3	1	2	LWSSP	Perlite	Sieved	8.3
18	2	3	1	2	SSP	Perlite	Granular	9.1
19	7	3	1	2	SSP	Perlite	Sieved	9.1
20	9	3	1	2	LWSSP	Light sand	Sieved	8.3
21	5	3	1	2	DCP	Perlite	Sieved	18.09
22	8	4	2	2	LWSSP	Perlite	Sieved	8.3
23	6	4	2	2	TCP	Perlite	Sieved	15.89
24	1	4	2	2	Nil-P	Perlite	-	0
25	3	4	2	2	LWSSP	Perlite	Granular	8.3
26	5	4	2	2	DCP	Perlite	Sieved	18.09
27	4	4	2	2	MCP	Perlite	Sieved	26.16
28	7	4	2	2	SSP	Perlite	Sieved	9.1

Table 9.6 Leaching column experiment visual observations and actions (2014). Single superphosphate (SSP), low water-soluble superphosphate (LWSSP), monobasic calcium phosphate (MCP), dibasic calcium phosphate (DCP) and tribasic calcium phosphate (TCP).

Date	Notes	Actions
13 Jan.	Columns potted up as per protocol and first watering of 3 litres to wash and clean medium conducted. Perlite samples (3) taken to the lab for analysis (Rowan Maddern and Brad Smith).	Potting up
15 Jan.	Columns watered with 2 L of water each. Will clean leachate bags out next watering on Friday the 17th.	Watering
17 Jan.	Clean leachate bags out and applied 3 litres of demineralised water per column to keep wetting them up and clean any more dust out. Watering was conducted using a small watering can allow even application through the free draining perlite. Put the columns in the right position as design. Ground and shelved all fertilisers using the grinder in the fertiliser lab at Kwinana to separate the fertiliser between 75 and 150 microns. Fertilisers were SSP, LWSSP, MCP, DCP and TCP Photos taken (Rowan Maddern and Brad Smith).	Watering Grinding and shelving
20 Jan.	Columns bags emptied and samples taken for a baseline of P from them. Fertilisers weighted out and applied to the surface of the medium. 1.5 L of demineralised water added to begin the experiment. The fertiliser looked to disappear from the surface on all columns and be wasted into the medium. Photos were taken (Rowan Maddern and Brad Smith).	Samples were taken – (baseline) Fertiliser applied and watering
22 Jan.	Samples collected from all columns but 25 as it was missed in the last watering. Brad will collect that single pot tomorrow and water it again to catch it up to the rest of the experiment. Columns watered (Rowan Maddern and Brad Smith).	Samples taken (84 mm) Watering
24 Jan.	Samples collected from all columns and watered. Samples dropped off at the lab (Rowan Maddern and Brad Smith).	Samples taken (168 mm) Watering
28 Jan.	Samples collected from all columns and watered (Rowan Maddern and Brad Smith).	Samples taken (252 mm) Watering
29 Jan.	Samples collected from all columns and watered. Sample from column 8 is missing (Rowan Maddern and Brad Smith).	Samples taken (336 mm) Watering
31 Jan.	Samples collected from all columns and watered. Dave Mathews has come and taken some photos for the next article, watercolour from the light sandy pots is starting to lighten up (Rowan Maddern and Brad Smith).	Samples taken (420 mm) Watering

Date	Notes	Actions
3 Feb.	Samples collected from all columns and watered (Rowan Maddern and Brad Smith).	Samples taken (504 mm) Watering
5 Feb.	Samples collected from all columns and watered (Rowan Maddern and Brad Smith).	Samples taken (588 mm) Watering
7 Feb.	Samples collected from all columns and watered. Column 18 had 2 watering's and so the result will need to be doubled (total P) (Rowan Maddern and Brad Smith).	Samples taken (672 mm) Watering
10 Feb.	Samples collected from all columns and watered (Rowan Maddern, Brad Smith).	Samples taken (756 mm) Watering
12 Feb.	Samples collected from all columns and watered (Rowan Maddern and Brad Smith).	Samples taken (840 mm) Watering
14 Feb.	Samples collected from all columns. Experiment finished and columns left as per design in case additional watering is required (Rowan Maddern and Brad Smith).	Samples taken (924 mm) Watering
28 Feb.	Pulled apart column 5 as per protocol and removed Perlite for testing as a test to find out if the system will work. Photos were taken (Rowan Maddern and Brad Smith).	Residual P removal from columns
1–11 Apr.	All Perlite columns pulled apart and sieved into sections of less than 2.2 mm, 2.2–4 mm, greater than 4 mm and the bottom 10% of the column. All particle sizes accept greater than 4 mm were tested as a whole and greater than 4 mm was mixed, and subsampled. The bottom was washed out and oven dried, and the other samples were air dried in aluminium dished. The samples were weighed and then tested for total P. Photos taken, (Rowan Maddern and Brad Smith).	Column testing to find residual P

9.3.2.1 Product solubility calculations

Properties:

i) Mono calcium phosphate
mw: 234.05 g/mol
ksp: n/a: soluble

ii) Di calcium phosphate
Mw(anhydrous): 136.06 g/mol
Ksp: 1 multiplied by $10^{-6.9}$

* There are two stable forms of Dical but their solubilities are similar.

Mw(dehydrate): 172.09 g/mol

Ksp: 2.77 multiplied by 10^{-7}
1 multiplied by $10^{-6.95}$

* More than are group has measured the ksp and values are different but similar.

* There is no accepted 'correct one' but take the first as being ok.

iii) Tri calcium phosphate $Ca_3(po_4)_2$
Mw: 310.17 g/mol
Recorded ksps
α): 1 multiplied by $10^{-25.5}$
1.3 multiplied by 10^{-26}
b): 1 multiplied by $10^{-28.9}$
2 multiplied by 10^{-29}
2.07 multiplied by 07 multiplied by 10^{-3}

* Tri calcium phosphate has a number of stable forms and they have different solubilities. The α form is the most stable and the most common.

The variances in the values show how difficult it is to measure the solubility of a very insoluble material.

Dissolution:

1) Mono calcium phosphate
Dissolve in water:

$Ca\ (H_2PO4)_2 \leftrightarrow (Ca^2+) +2(H_2PO4)$

1 mol = 1 mol added 2 mols

Assume 10 g material:

Mols Mono calcium Phosphate $= \frac{\text{Mass product}}{\text{Mw product}}$

$= \frac{10\text{ g}}{234.05}$

= 0.04275 mols

Mols of phosphate in solution = 0.04275 multiplied by 2

= 0.0845 mol

Note: mw of P: 30.97

% of P in Mono calcium Phosphate: 26.46%

= mols of phosphate in solution moles = concentration of P

= N = C.V (conc. Volume)

Assume tank vol HOL $C = \frac{N}{V}$

$= \frac{0.0545}{40}$

= 0.002136 mol L^{-1}

Conc of P: g/L = 0.002136 multiplied by 30.97

= 0.06616 g/L

= 66.161 mg/L or ppm

2) Di calcium phosphate

As dical is insoluble its dissolution is governed by its solubility product:

For a product example in equilibrium:

$Ca\ (HPO_4)_{(5)} \rightarrow [Ca^{2}+]\ [HPO_4^{-}]$

The equilibrium constant K =

$$K \quad = \quad \frac{[Ca^{2}+]\ [HPO_4^{-}]}{[Ca(HPO_4)]}$$

But for solids $[Ca(HPO_4)] = 1$

$K \quad = \quad [Ca^{2}+]\ [HPO_4^{-}]$

In this instance K = Ksp = solubility product.

For the Dihydrate Ksp = 2.77 multiplied by 10^{-7}

$[HPO_4]\ [Ca^{2}+]$ = 2.77 multiplied by 10^{-7}

$[\times]\ [\times]$ = 2.77 multiplied by 10^{-7}

$\times^{2}$ = 2.77 multiplied by 10^{-7}

$[\times] = [HPO_4^{-}]$ = $\sqrt{2.77}$ multiplied by 10^{-7}

= 5.26 multiplied by $10^{-}4$ mol L^{-1}

The concentration of P in solution = 5.26 multiplied by 10^{-4} mol L^{-1}

Concentration in mass (g/L) = 5.26 multiplied by 10^{-4} multiplied by 30.97

= 0.0163 g/L

= 16.30 mg/L or ppm

Starting amount: 10 g

Mw dical: 172.09 g/mol

Mols = m/mw

= 10/172.09

= 0.058109

0.058109 moles of P at the start

The concentration of P in solution is 5.26 multiplied by 10^{-4}

Mols of P = CV

= 5.26 multiplied by 10^{-4} 40 L

= 0.0210

Theoretically: 36.2% of the Dical dissolves rapidly is available.

As P is removed from the system the remaining dical will dissolve as required.

3) Tri calcium phosphate

Its dissolution is also governed by its product solubility product.

Ksp = $[Ca_3\,(DO4)_2]$ = $3[Ca^{2}+]+2[PO4^{3-}]$

= $[Ca_3\,(DO4)_2]$ = $[Ca^{2}+]^3\,[PO4^{3-}]^2$

1.3 multiplied by 10^{-26} = $[\times]^3\,[\times]^2$

1.3 multiplied by 10^{-26} = $\times 5$

× = $5\sqrt{1.3}$ multiplied by 10^{-26}

= 5.7008 multiplied by 10^{-13}

The phosphate concentration in solution will be 2 × = 1.140 multiplied by 10^{-12} mol^{-1}

Concentration in mass g/L = 1.140 multiplied by 10^{-12} ×30.97

= 3.531 multiplied by 10^{-11} g/L

or 3.531 multiplied by 10^{-8} ppm

Very little dissolves, the rate of P in solution is dictated by how quickly it is removed.

If starting amount = 10 g

Mw tri calcium phosphate: 310.17 g/mol

Moles = mass/mw

= 10/310.17

= 0.0322 moles

= 0.0322 multiplied by 2 moles of P at the start

= 0.0644 moles of P

Amounts of dissolution = $\dfrac{1.140 \text{ multiplied by } 10^{-12}}{0.0644}$

= Nothing.

9.3.3 Pot experiment notes and attachments

Table 9.7 Full experimental design (2012). Single superphosphate (SSP) and low water-soluble superphosphate (LWSSP).

Plot no.	Bench	Section	Row	Plot	Species	Soil	Fertiliser
101	1	1	1	1	Clover	Heavy	LWSSP
102	1	1	2	2	Clover	Light	SSP
103	1	1	3	3	No plants	Light	LWSSP
104	1	1	4	4	Ryegrass	Heavy	LWSSP
105	1	1	5	5	Ryegrass	Heavy	SSP
106	1	1	6	6	Ryegrass	Medium	SSP
107	1	1	7	7	Clover	Heavy	Nil-P
108	1	2	1	8	Ryegrass	Light	SSP
109	1	2	2	9	No plants	Medium	LWSSP
110	1	2	3	10	No plants	Heavy	SSP
111	1	2	4	11	No plants	Light	Nil-P
112	1	2	5	12	Ryegrass	Medium	LWSSP
113	1	2	6	13	No plants	Heavy	LWSSP
114	1	2	7	14	Clover	Heavy	SSP
115	1	3	1	15	Ryegrass	Heavy	Nil-P
116	1	3	2	16	No plants	Medium	Nil-P
117	1	3	3	17	No plants	Light	SSP
118	1	3	4	18	Ryegrass	Light	Nil-P
119	1	3	5	19	Clover	Medium	LWSSP
120	1	3	6	20	Clover	Light	Nil-P
121	1	3	7	21	Clover	Medium	Nil-P
122	1	4	1	22	Clover	Medium	SSP
123	1	4	2	23	Ryegrass	Light	LWSSP
124	1	4	3	24	Ryegrass	Medium	Nil-P
125	1	4	4	25	Clover	Light	LWSSP
126	1	4	5	26	No plants	Medium	SSP
127	1	4	6	27	No plants	Heavy	Nil-P
201	2	1	1	1	Clover	Light	LWSSP
202	2	1	2	2	Ryegrass	Light	LWSSP
203	2	1	3	3	Ryegrass	Heavy	LWSSP
204	2	1	4	4	No plants	Light	Nil-P
205	2	1	5	5	No plants	Medium	Nil-P
206	2	1	6	6	No plants	Medium	SSP
207	2	1	7	7	Ryegrass	Medium	Nil-P
208	2	2	1	8	Clover	Light	SSP
209	2	2	2	9	No plants	Heavy	Nil-P
210	2	2	3	10	Clover	Medium	Nil-P
211	2	2	4	11	Clover	Medium	SSP
212	2	2	5	12	Clover	Medium	LWSSP
213	2	2	6	13	No plants	Heavy	SSP
214	2	2	7	14	Ryegrass	Medium	SSP

Plot no.	Bench	Section	Row	Plot	Species	Soil	Fertiliser
215	2	3	1	15	Clover	Heavy	SSP
216	2	3	2	16	Clover	Heavy	LWSSP
217	2	3	3	17	No plants	Heavy	LWSSP
218	2	3	4	18	Ryegrass	Light	SSP
219	2	3	5	19	Ryegrass	Heavy	SSP
220	2	3	6	20	Ryegrass	Light	Nil-P
221	2	3	7	21	Clover	Light	Nil-P
222	2	4	1	22	No plants	Light	SSP
223	2	4	2	23	No plants	Medium	LWSSP
224	2	4	3	24	Clover	Heavy	Nil-P
225	2	4	4	25	Ryegrass	Heavy	Nil-P
226	2	4	5	26	Ryegrass	Medium	LWSSP
227	2	4	6	27	No plants	Light	LWSSP
301	3	1	1	1	Clover	Medium	SSP
302	3	1	2	2	No plants	Medium	SSP
303	3	1	3	3	Clover	Light	LWSSP
304	3	1	4	4	No plants	Heavy	Nil-P
305	3	1	5	5	No plants	Medium	Nil-P
306	3	1	6	6	Clover	Heavy	LWSSP
307	3	1	7	7	Ryegrass	Heavy	SSP
308	3	2	1	8	No plants	Heavy	LWSSP
309	3	2	2	9	No plants	Medium	LWSSP
310	3	2	3	10	Clover	Heavy	Nil-P
311	3	2	4	11	No plants	Heavy	SSP
312	3	2	5	12	Clover	Light	Nil-P
313	3	2	6	13	Ryegrass	Heavy	Nil-P
314	3	2	7	14	Ryegrass	Heavy	LWSSP
315	3	3	1	15	Ryegrass	Light	Nil-P
316	3	3	2	16	Ryegrass	Light	SSP
317	3	3	3	17	No plants	Light	Nil-P
318	3	3	4	18	Clover	Heavy	SSP
319	3	3	5	19	Ryegrass	Light	LWSSP
320	3	3	6	20	No plants	Light	LWSSP
321	3	3	7	21	Ryegrass	Medium	SSP
322	3	4	1	22	Clover	Medium	LWSSP
323	3	4	2	23	No plants	Light	SSP
324	3	4	3	24	Ryegrass	Medium	LWSSP
325	3	4	4	25	Ryegrass	Medium	Nil-P
326	3	4	5	26	Clover	Light	SSP
327	3	4	6	27	Clover	Medium	Nil-P

Table 9.8 Visual observations (2012).

Date	Notes	Action
16 Oct.	Dropped all soils and supplies out at South Perth. I have also soil taken 3 soils samples from each soil type and random from the bags as well as 3 samples from the fertilisers (Rowan Maddern).	Preparation
17 Oct.	Pot up all three soils types and completed design, the heavy soil had 1.4 kg applied to each pot, and the medium and light soils had 2.0 kg applied to each pot. The heavy soil only had 1.4 kg applied because of the bulk density and the volume was greater than the other two types. Each pot was filled to the bottom inner ring of the pots. Layout out an experiment in a glass house with plastic bags underneath each pot and applied 300 mL of demineralised water to each pot to soak in. Photos were taken and (Rowan Maddern, Dean Diepeveen and Deb Pritchard). Bench layout was: 3 rows of 7 pots and a row of 6 pots. Pot 1 was located on the top of the bench next to the wall, and each row started that way. The row of 6 pots stopped at the normal position on the other rows leaving the seventh spot empty. Bench 3 was to the north-west; bench 1 was located next to bench 1 on the same side to the north east. Bench 2 was located by itself to the south-east in a direct line with bench 1. Bench 3 was located next to the air conditioner and was in the sun more; this could affect the outcome and results of the experiment (Rowan Maddern and Dean Diepeveen).	Preparation Potting Setting up
19 Oct.	Added trace element mixture (A, B, and C) at 1.67 mL per kg of soil with Alsoca inoculants at 10 grams per 20 L of water. The mixtures were added with 346 mL of DM water to make up to the 646 mL or 50 mL of rainfall. The heavy soil type was watered first, and then another batch was made up for the medium and light soils types. The light and medium soils have reached field capacity, and soil leachate has come through to the leaching bags. The heavy soil type still has not started to leach. The light soil has leached the most, followed by the medium as would be expected. All pots were seeded as per design with 20 seeds per plot and will be thinned to 10 plants after germination. The heavy soil type was seeded first followed by the light and medium. Seeding was conducted by using a pair of tweezers and dropping a single seed into each hole from a cup of seeds. The seed depth was to a maximum of 10 mm below the surface of the soil and demineralised water was misted using a garden pressure sprayer over the soil to close the holes. Photos were taken (Rowan Maddern and Dean Diepeveen).	Nutrient solution Watering Seeding Photos

Date	Notes	Action
26 Oct. *(0 DAS)* *Growth block 1*	For the last week, the pots have been misted once a day. Due to low seed germination in some pots, mostly the heavy clays all plants were removed and all pots reseeded. The pots were reseeded by scratching the soil surface to a depth of about 5 mm and then added seed to the surface. The seed was added until the pot was even on the surface and then the pots were missed, and the surface levelled again. The surface seed was then incorporated a little bit by hand. Pots will be misted for another week and then thinned and fertiliser added. Photos were taken (Rowan Maddern and Dean Diepeveen).	Experiment start Photos
1 Nov. *(6 DAS)* *Growth block 1*	Checked pot with Brad Smith, some have come up very well, but some are still slow mainly clover pots. We have thinned out some of the pots that have good plant numbers to reduce the numbers but will have to thin again to get back the target of ten plants. Pots 301, 303, 306, 312, 310, 322, 326, 327, 102, 119, 120, 121,122 and 125 are very slow to germinate. All clover on bench 2 has a good germination. Will come back on Monday and check again and may add P to pots. I have misted them twice today once before thinning and once after to build up soil moisture. Photos were taken (Rowan Maddern and Brad Smith).	Photos
2 Nov. *(7 DAS)* *Growth block 1*	Weighted out all P application into small containers and combined them with the Urea. LWSSP was weighted out at 0.399 g, SSP, at 0.365 g and urea at 0.143 g +/- 0.020 g. Photos were taken (Rowan Maddern).	P Fertiliser applied Photos
5 Nov. *(10 DAS)* *Growth block 1*	Thinned the pots back to between 10–15 plants and will thin again once they are bigger. Added the P and N fertiliser to the surface of all pots and added 300 mL of water to start the experiment. For the first two harvest the watering program will be: Monday: 300 mL of water (23.2 mm rainfall). Tuesday: 346 mL of water 26.8 mm of rainfall). Wednesday: collect leachate and add 300 mL of water. Thursday: 346 mL of water. Friday: Collect leachate plus mist or add small amounts of water. Photos were taken and Jake the casual will be in charge of watering and collection. A collection of leachate will be conducted by removing the bags, taking a weight of the liquid and then a subsample for lab analysis from all pots (Rowan Maddern and Dean Diepeveen).	Thinning pots
9 Nov. *(14 DAS)* *Growth block 1*	Dean and Jackson have finished thinning the pots back to 10 plants and have taken the first two leaching samples (Rowan Maddern).	Thinning pots

Date	Notes	Action
18 Nov. *(23 DAS)* *Growth block 1*	Thinned the pots for the last time today to around 10 plants and misted the pots twice. Pots will not be watered on Monday and will get the total 646 mL on Tuesday. Brad picked up the first weeks leachate samples last week (14 Nov.), and I have collected the second weeks today. They will get analysed for total P using the ICP test. I have taken photos, and there may be a slight P response and super maybe ahead. I have also picked up the leaching weight data and will input the data (Rowan Maddern).	Thinning pots
23 Nov. *(27 DAS)* *Growth block 1*	Jackson has collected week 3 worth of leachate samples, and I have helped on the 300 mm rainfall collection that I have dropped at the lab today. Plants are growing well, and I do not want to thin them anymore. We will need to add the trace element mixture again soon. Dean has arranged to have the pots misted on Sundays to stop the pots from drying out. Photos were taken (Rowan Maddern).	Photos taken
7 Dec. *(42 DAS)* *Growth block 1*	Good P response to both LWSSP and super with the heavy soil type looking the best. But visual response across all three soil types. LWSSP looks to be better on light soil type than super. Leachate samples taken to the lab for the last two weeks and ryegrass looks a bit low on n and will look at adding urea ammonium nitrate-NS to all pots along with the trace element mixture next week. Will do harvest 1 Monday next week, photos taken (Rowan Maddern).	Photos taken
10 Dec. *(45 DAS)* *Growth block 2*	Conducted first harvest from all pots with plants in them. Photos were taken before cutting each pot. Plants were cut to about 1 cm height placed into paper bags and then wet weights taken from each pot. Paper bags were taken to the lab for dry matter weights and then I may have to bulk the three reps together for analysis. Added a basal trace element mixture as per start of experiment and 50 L/ha N and 8 L/ha S in the form of urea ammonium nitrate-NS as well (Rowan Maddern).	Harvest 1 Nutrient solution applied
12 Dec. (*47 DAS)* *Growth block 2*	Leachate collected, and 300 mL of water added. Photos were taken, and plants are growing well after harvest. Ryegrass is coming back the best. Nil plant pots with the heavy soil type had a green moss growing on the surface (Rowan Maddern and Dean Diepeveen).	
14 Dec. *(49 DAS)* *Growth block 2*	Leachate collected and pots misted after collection. Pots are growing strong with good P responses on all soil types but best on heavy. Heavy soil may have held on to P better while still allowing the volume of water to flow down the profile. Single superphosphate and LWSSP look about the same visually, and clover on the lighter soil types is starting to look p hungry. Photos were taken (Rowan Maddern and Dean Diepeveen).	Photos taken

Date	Notes	Action
19 Dec. *(54 DAS)* *Growth block 2*	Leachate collected and pot watered with 300 mL per pot plus nutrient solution and urea ammonium nitrate sulphur mixture. Photos were taken (Rowan Maddern and Dean Diepeveen).	Nutrient solution added Photos
21 Dec. *(56 DAS)* *Growth block 2*	Leachate collected and pots misted. Good visual responses to LWSSP and SSP in both ryegrass and clover. LWSSP maybe a head on heavy soil now. Nil-P pots with both clover and ryegrass are now dropping away. Next week the watering is being reduced to 50 mm per week (two watering) and a single leachate collection. 300 mL early in the week and 346 mL later in the week with leachate collected on Friday. Photos were taken (Rowan Maddern and Dean Diepeveen).	Photos
24 Dec. (56 DAS) *Growth block 2*	Pots watered with 300 mL of demineralised water, may need to harvest on Friday or Monday next week. Photos were taken (Rowan Maddern).	
27 Dec. (59 DAS) *Growth block 2*	Water plants with 346 mL per pot, they look very dry as it very hot (Rowan Maddern and Dean Diepeveen).	
28 Dec. (60 DAS) *Growth block 2*	Leachate collected and pots misted, leachate may have evaporated because it is so hot; this will have to be allowed for. Harvest 2 conducted, will add nutrient solution mixture on Monday. Photos were taken (Rowan Maddern, Dean Diepeveen).	Harvest 2 Photos Nutrient solution
31 Dec. (66 DAS) *Growth block 3*	Watered plants with 300 mL of water plus nutrient solution mixture. Good plant growth since harvest, photos were taken (Rowan Maddern).	
Field experiment 4 visual observations: (2013)		
3 Jan. (66 DAS) *Growth block 3*	Watered pot with 346 mL and they were misted between the last watering. Photos were taken (Rowan Maddern).	Photos
4 Jan. (70 DAS) *Growth block 3*	Leachate collected, and pots misted, photos taken. The experiment will finish on the 17 of Jan. Still got phosphorus response and nil looking very low for dry matter yield production (Rowan Maddern and Dean Diepeveen).	
11 Jan. (77 DAS) *Growth block 3*	Leachate collected, and pots misted, photos taken. So plants starting to look P-deficient and burnt tips on the ryegrass pots. Checked the data from the first harvest tissue analysis and it looks potassium and nitrogen deficient, and this may have limited the response, but it still had good P uptake and growth data (Rowan Maddern, Dean Diepeveen and James Easton).	

Date	Notes	Action
18 Jan. (84 DAS) *Growth block 3*	Leachate collected and harvested 3 conducted. Pots taken to the lab to have the roots sieved and removed for analysis (dry matter yield) and phosphorus concentration and soil samples taken. Photos were taken, and this experiment is now finished (Rowan Maddern and Dean Diepeveen).	Harvest 3 Photos
13–15 Feb. Post experiment Soil and roots analysis CSBP lab (Bibra Lake)	Note: some pot on the heavy soil type may have reduced root weights because it was a trial and error method to try and remove the roots. The roots were first dry sieved, then was in the small amount of demineralised water, then washed in shade cloths and then finally washed with tap water over a 2 mm screen (most pots). Light and medium soils: (step 1) Pots were tipped upside down and placed in an aluminium tray. The soil placed on its side with the top of the pot away towards the middle of the bench. The total length of the soil is 12 cm. The soil was then split down the middle using an implement and two-sided opened up. The soil was then broken up using the implement for the top 10 cm of the pot and bottom 2 cm avoided. 400 grams of soil is then placed into another tray and then screened over a 2 mm screen. The roots removed and the soil mixed up and placed into a soil sampling bag. The roots were then collected from the top of the screen and placed into a paper bag. (Both bags numbered with the pot number.) The rest of the soil was then screened through a 2 mm screen and the roots removed into the paper bag and the rest of the soil discarded. Heavy soil: (step 1) Pots were tipped upside down and placed in an aluminium tray. The soil placed on its side with the top of the pot away towards the middle of the bench. The total length of the soil is 12 cm. The soil was then split down the middle using an implement, and two-sided opened up. The soil was then broken up using the implement for the top 10 cm of the pot and bottom 2 cm avoided. 400 grams of soil is then placed into another tray and then screened over a 2 mm screen. The roots removed and the soil mixed up and placed into a soil sampling bag. The roots were then collected from the top of the screen and placed into a paper bag. (Both bags numbered with the pot number.) The rest of the soil was then placed onto a 2 mm screen and washed with tap water until all soil was removed and the roots placed into the paper bag.	Post soil analysis

Date	Notes	Action
	Washing roots all soil types: (step 2) All roots were removed from the paper bag and then washed with DI water in a tray to remove all soil and any minerals from the tap water and then placed back into the paper bags. Soil and root analysis: All roots were then dried for dry matter weights and then for P analysis, all soils were then tested for P (Colwell), total phosphorus, pH, etc. (Rowan Maddern).	

Table 9.9 Water is holding capacity for the light, medium and heavy soils.

		Wet	Dry (38°C)	(Wet-Dry)/Dry	
Soil type	**Pot**	**5 April**	**7 April**		**%**
Heavy	1	134.2	97.5	0.376	37.6
Heavy	2	158.4	112.8	0.404	40.4
Heavy	3	167.6	126.4	0.326	32.6
Average		**153.4**	**112.2**	**0.4**	**36.9**
Medium	1	121.3	101.9	0.190	19.0
Medium	2	148.8	117.8	0.263	26.3
Medium	3	158.9	127.8	0.243	24.3
Average		**143.0**	**115.8**	**0.2**	**23.2**
Light	1	132.9	111.3	0.194	19.4
Light	2	126.5	109.9	0.151	15.1
Light	3	134.6	110.4	0.219	21.9
Average		**131.3**	**110.5**	**0.2**	**18.8**

9.3.3.1 Leachate volume analysis data

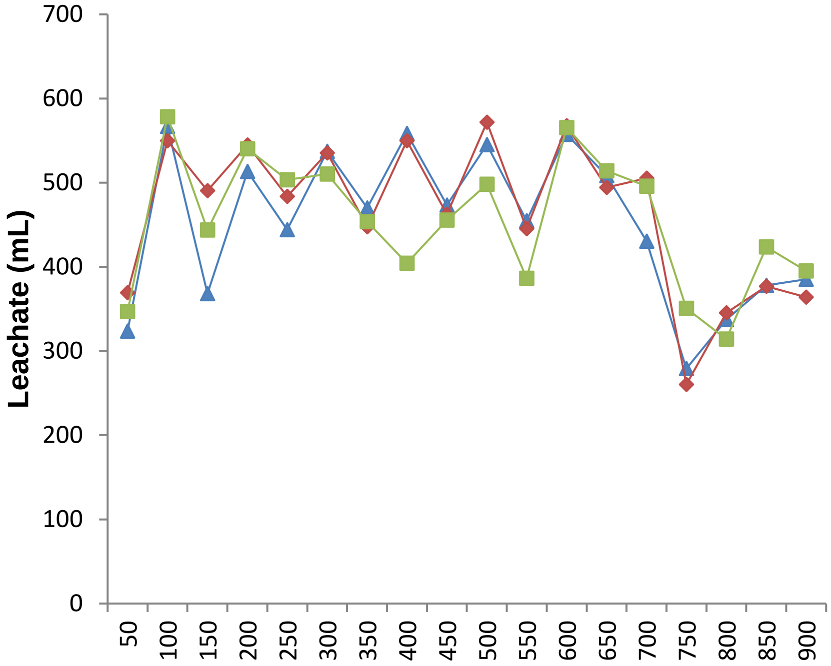

Figure 9.1 Light soil no species – leachate volume in vs volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

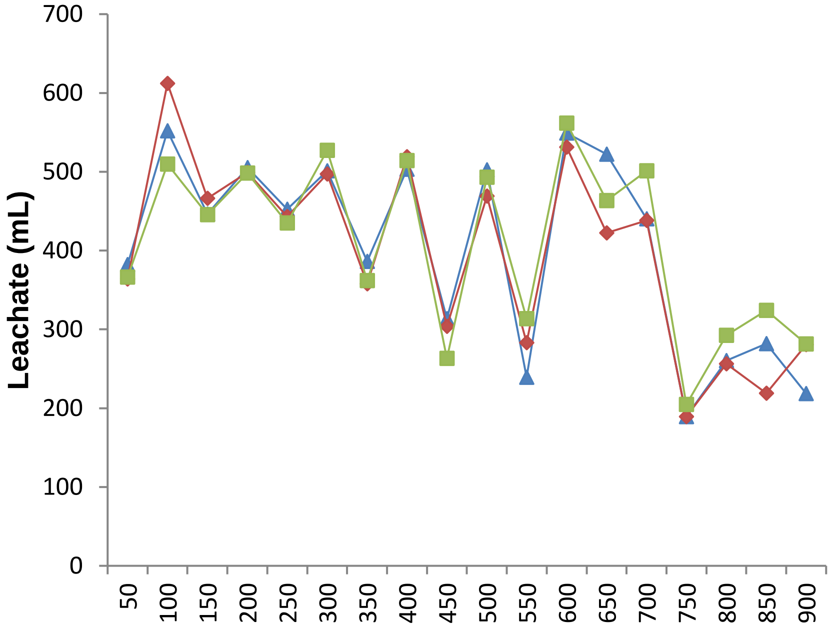

Figure 9.2 Light soil clover – leachate volume in vs volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

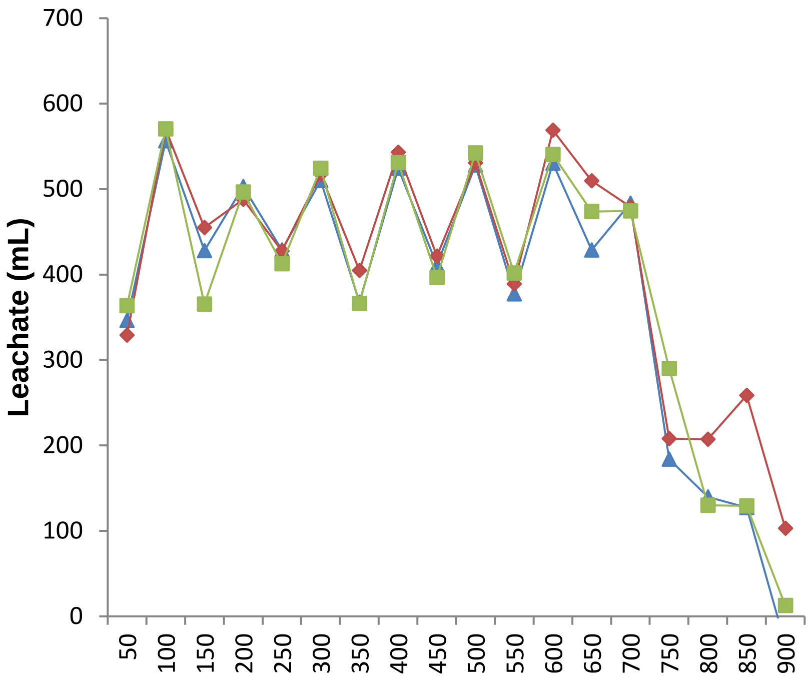

Figure 9.3 Light soil ryegrass – leachate volume in vs volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

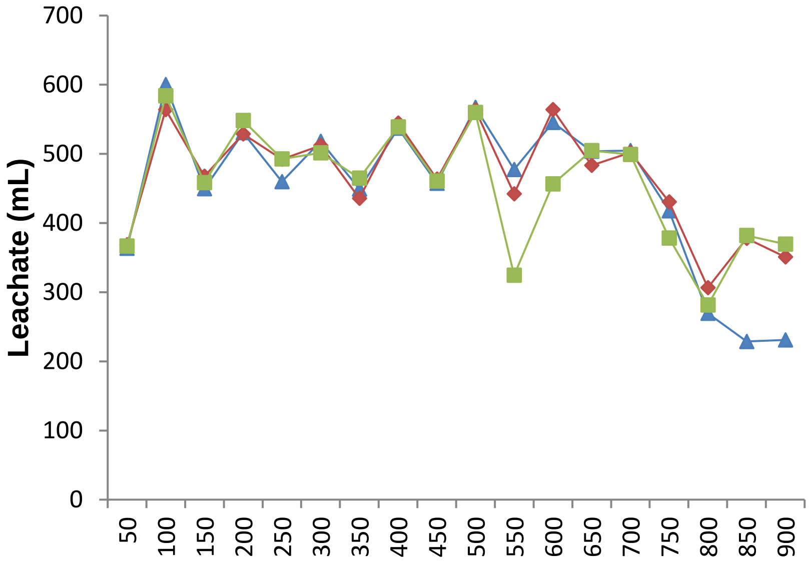

Figure 9.4 Medium soil no species – leachate volume in vs volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

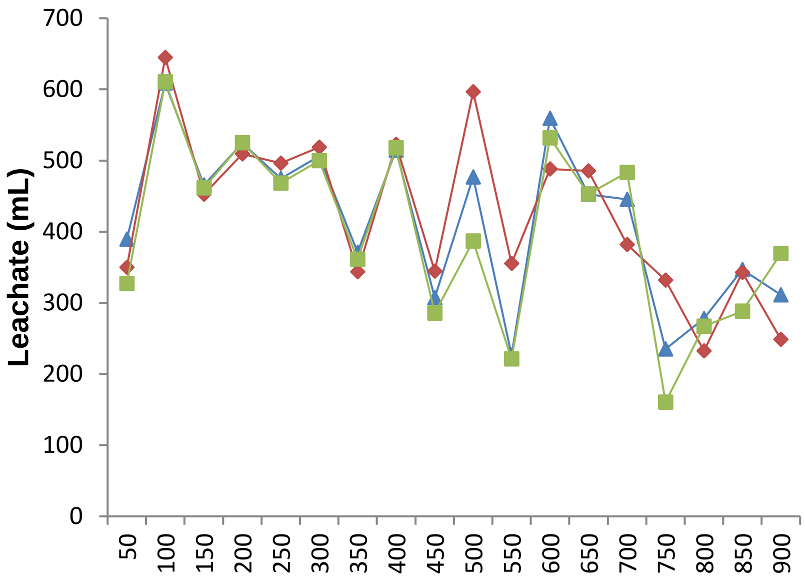

Figure 9.5 Medium soil clover – leachate volume in vs. volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

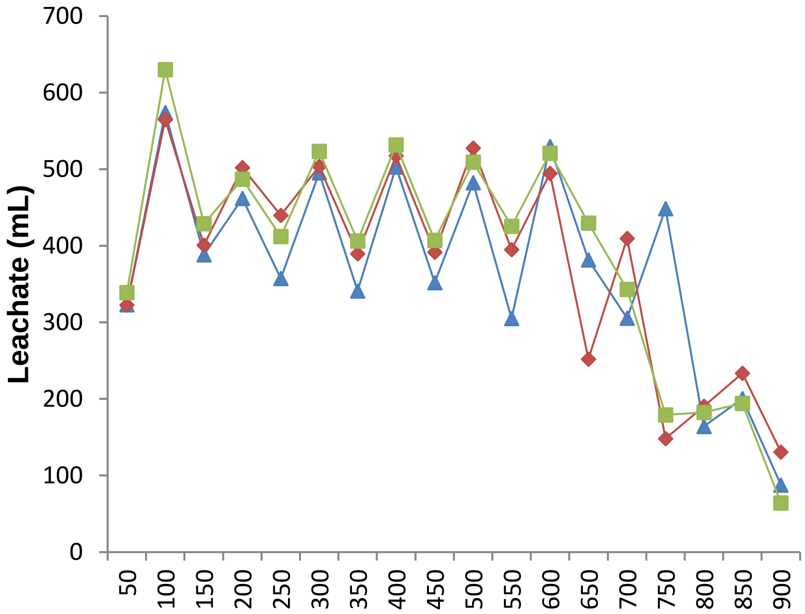

Figure 9.6 Medium soil ryegrass – leachate volume in vs. volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

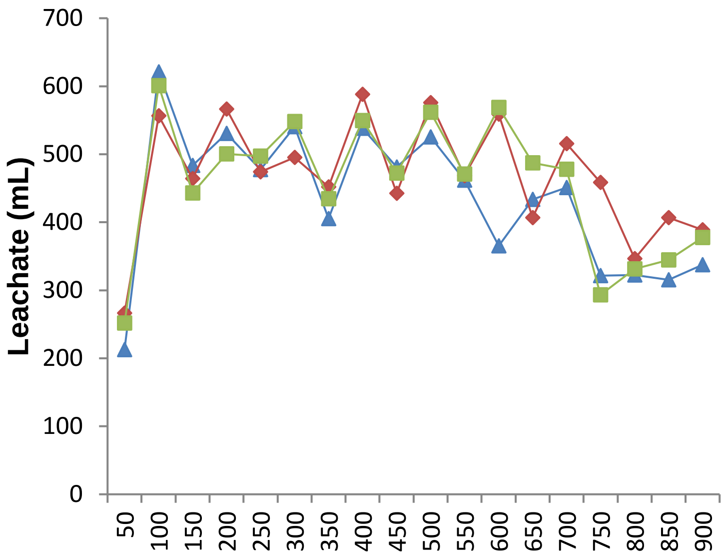

Figure 9.7 Heavy soil no species – leachate volume in vs. volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

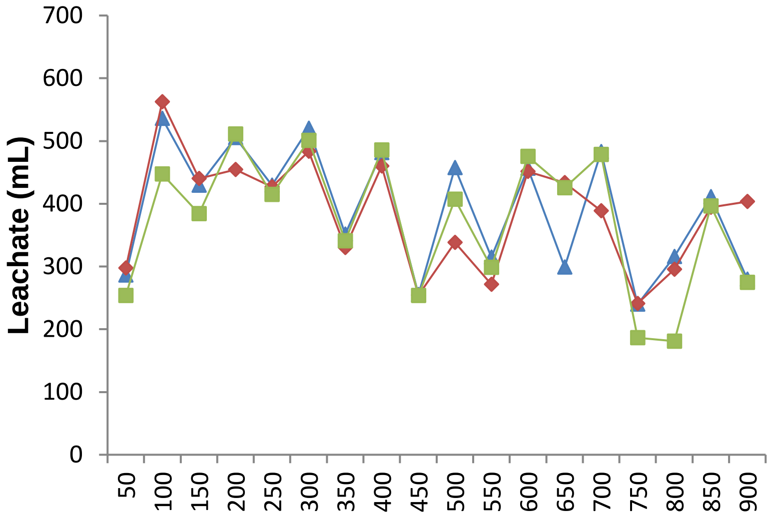

Figure 9.8 Heavy soil clover – leachate volume in vs. volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

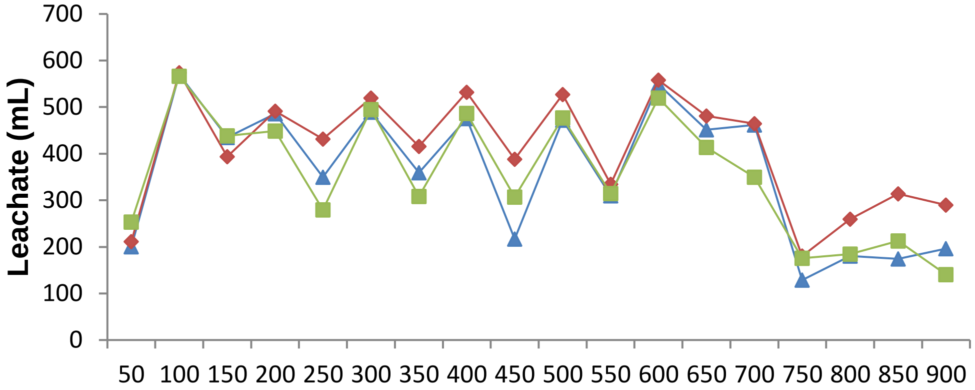

Figure 9.9 Heavy soil ryegrass – leachate volume in vs. volume of simulated rainfall (mm). □ single superphosphate, Δ low water soluble superphosphate and ◊ nil-phosphors control.

9.3.4 Field experiment notes and attachments

Table 9.10 Field experiment equipment description and uses.

Equipment	Description and uses
Cone top dresser	A machine designed around two fibreglass cones that place fertiliser into a belt for the even distributions of granular fertiliser. The fertiliser is then placed into a venturi and up to a distribution head and via 8 tubes onto the ground. The machine is calibrated for a plot length of 38 m and the rate applied can be varied depending on what is required. This machine was used to spread the lime, basal fertilisers and fertiliser treatments.
Spray motorbike	A machine designed for the even application of liquids and is a four-wheel quad bike with a spray system mounted onto its frame. This was used to apply all herbicide, pesticides and liquid basal fertilisers.
Post hole digger	A machine designed to dig holes for the placement of copper treated logs into the ground for fencing and exclusion of stock from field experiment locations. This machine was used to place 6 copper treated logs around each field experiment site 3 at each end, one at the front, middle and the end.

9.3.4.1 Field experiment site-1

Table 9.11 Full experiment design (2009–2011).

Plot	Trt	Fertiliser	P kg/ha
1	6	Low water-soluble superphosphate	15
2	2	Low water-soluble superphosphate	5
3	3	Single superphosphate	5
4	4	Low water-soluble superphosphate	10
5	9	Single superphosphate	25
6	8	Low water-soluble superphosphate	25
7	5	Single superphosphate	10
8	1	Nil-P	0
9	7	Single superphosphate	15
10	1	Nil-P	0
11	2	Low water-soluble superphosphate	5
12	3	Single superphosphate	5
13	4	Low water-soluble superphosphate	10
14	5	Single superphosphate	10
15	6	Low water-soluble superphosphate	15
16	7	Single superphosphate	15
17	8	Low water-soluble superphosphate	25
18	9	Single superphosphate	25
19	3	Single superphosphate	5
20	8	Low water-soluble superphosphate	25
21	1	Nil-P	0
22	2	Low water-soluble superphosphate	5
23	4	Low water-soluble superphosphate	10
24	7	Single superphosphate	15
25	6	Low water-soluble superphosphate	15
26	5	Single superphosphate	10
27	9	Single superphosphate	25

Table 9.12 Visual observations (2009).

Date	Notes	Action
15 May	The trial was pegged and top dressed as per design. The site had 2.2 t/ha of lime applied. The site had 7 kg/ha Balansa clover top dressed over the site and the fencing posts were put in. The soil sample was taken from 0 to 70 cm and photos was taken (Rowan Maddern and Ryan Guthrie).	Experiment pegged Seeded Soil samples Photos
19 May	Site sprayed with 250 mL/ha Telstar using the motorbike (Rowan Maddern).	Spraying
22 June	The trial was sprayed with 100 mL/ha Lemat and 600 mL/ha MCPA. Not much clover but good grass and large amounts of capeweed. Good soil moisture but no visual response. Photos were taken and est. 0.5 t/ha dry matter yield. Solar panel had been blown over a few times and fixed by the farmer (Rowan Maddern).	Spraying Photos
23 July	The site had the fence dropped and grazed by the cows. Photos were taken and no response yet (Rowan Maddern and Ryan Guthrie).	Photos
31 July	The site had the front section fenced up, no signs of pest or weeds. Est. 500 kg/ha dry matter yield (Rowan Maddern and James Easton).	Fencing
3 Sept.	Cows had got into the trial and chewed up the leads for the power pack. Still good visual responses to the high rate of super, est. 1 t/ha dry matter yield difference between nil plots and 25 P kg/ha plots. Taken 3 grab samples from Nil, 25 SSP and 25 LWSSP plots in the first rep. Photos were taken, and the fence is hocked up with a new power pack (Rowan Maddern and Ryan Guthrie).	Tissue sampling Photos
8 Sept.	The fence is still up, and gardens hose put onto tape touching the copper logs (Rowan Maddern).	Fencing
1 Oct.	The trial had 30 plates taken across the whole trial and grab samples taken. Photos are taken from the first rep. Looks like the LWSSP maybe ahead of the SSP, Ryan will do fencing next week (Rowan Maddern and Ryan Guthrie).	DMY measurement Tissue sampling Photos
9 Oct.	Applied 80 kg/ha muriate of potash down every plot (plot by plot). Fences rolled up (cattle will be out for the rest of the season). Background area tightly grazed to 300 kg/ha or so. Estimated dry matter yield in fenced off section plots range from 1.0 to 2.2 t/ha. Little bug activity and/or damage (James Easton and Ryan Guthrie).	Fertiliser Fencing

Table 9.13 Visual observations (2010).

Date	Notes	Action
14 Jan.	Trial soil sampled from nil-P and both 25 treatments. 1st rep also sampled the same treatments at 10–20 cm and 20–30 cm. The paddock was sampled for a possible move of the trial (Rowan Maddern).	Soil sampling
29 Mar.	Trial top-dressed with 200 kg/ha NS 3:1 and 150 kg/ha muriate of potash. The P applications, where spread by hand on the two blocks with plot 20, 21 in Block been top-dressed wrong and design, was fixed up. The site some perianal grasses growing and had 50 mm of rain 7 days ago. Grass at half leaf, clover at cotyledon (Rowan Maddern and Ryan Guthrie).	Fertiliser
30 Mar.	The trial had front block fenced up and photos taken (Rowan Maddern and Ryan Guthrie).	Fencing
17 June	Experiment sprayed with 120 L/ha FNS, 1.5 L/ha MCPA 500 and 200 mL/ha Lemat. Est. 1.0 t/ha dry matter yield with lots of capeweed present. Photos were taken, and the fence is up and operation (Rowan Maddern).	Spraying Photos Fencing
25 June	Mass of capeweed but still good responses. Ryegrass better at the eastern end. Keep N up to this trial also. Background not very well grazed at this stage. Measure in 7–10 days (Daniel Parnell).	
8 July	The experiment measured at 20 plates per plot, good visual response but the cows have got in. Measured front section (1–2) and taken 6 cuts. Will return next week and take photos and leaf samples. Cows are out of the paddock. The fence will need to be fixed and moved (Rowan Maddern).	DMY measurement
13 July	Experiment grabs samples taken for all of block 1 and 2. Moved the fence to the back section. Power not working so will fix on the 16/07/2010 but no cows in the paddock. Photos were taken (Rowan Maddern).	Tissue sampling Photos Fencing
16 July	Sprayed 120 L/ha urea ammonium nitrate sulphur over the trial and hooked up power pack (Rowan Maddern and Ryan Guthrie).	Spraying
27 Aug.	The site had front block measured at 15 plates per plot because the paddock had not been grazed. Looks to be good P response on the freshly applied section and 8 cuts were taken. 3 grabs samples were taken from nil-P and high SSP/LSWP plots in the first rep. Photos were taken (Rowan Maddern).	DMY measurement Tissue sampling Photos
30 Aug.	150 kg/ha muriate of potash applied by hand to all plots. Est. 1.5 t/ha dry matter yield in fenced section, but the site is very dry, and some grasses are setting seed. The cows have grazed the open section (Rowan Maddern and Doug Hamilton).	Fertiliser
22 Sept.	100% ryegrass. Cape weeds dead. Very dry. Ryegrass at soft dough. The trial is finished for this season. No responses (photos were taken) (Rowan Maddern and Ryan Guthrie).	Photos
21 Oct.	Fence rolled up, and pasture is setting seed (Rowan Maddern).	

Table 9.14 Visual observations (2011 and 2012).

Date	Notes	Action
21 Jan.	Soil sampled all plots from the front back block (0–10 cm) (54 Plots), site very bear photos taken. A = fresh, fertilisers 2010, B = residual fertiliser 2010 (Rowan Maddern).	Soil sampling
17 Mar.	Soil sampled (10–20) and (20–30) cm from nil-P and 25 kg/ha SSP/LWSSP plots. Site grazed well down and very dry. Photos were taken (Rowan Maddern).	Soil sampling Photos
4 Apr.	Top dressed SSP/LWSSP by hand and then used cone top dresser to applied 150 kg/ha of MOP and 150 kg/ha GSOA. The site is very dry and photos taken (Rowan Maddern and Andreas Neuhaus).	Fertiliser Photos
21 Apr.	Sowed trial using new pasture seeded with a mixture of 62.5% Balansa clover and 37.5% Goose sub clover @ 15 kg/ha. No soil moisture and the back section were fenced up with the hot wire. Photos were taken (Rowan Maddern and Ryan Guthrie).	Fencing Photos
3 June	Sprayed out 100 mL/ha Lemat, good soil moisture and some clover coming through after seeding the site. Not as much as I would have thought coming up. Some capeweed, est. 0.5 t/ha dry matter yield and photos were taken (Rowan Maddern).	Spraying Photos
22 June	Changed power pack, still no clover and Rob has put some cows in on the 23 of Jun (Rowan Maddern and Ryan Guthrie).	Fencing
11 July	The experiment is looking good and will need a measure soon. The top plot is about 2.3 t/ha dry matter yield. Some responses and visual scores done on both fresh and residual blocks. 12 mm in the rain gauge and there may be more Guilford grass in the residual section, pointing to better comp with fresh P. Background grazed well. Photos were taken (Rowan Maddern and Ryan Guthrie).	Photos
14 July	The experiment measured on both fresh and residual sections (back block) at 15 plates per plot, very grassy and little clover. Grab samples taken from all plots in both blocks and the first rep are the most responsive. Grab samples are all grass. Maybe a slight P response in the trial. Fence moved to the front section and photos taken. Est. Top plot had around 2–2.3 t/ha dry matter yield (Rowan Maddern and Ryan Guthrie).	DMY measurement Tissue sampling Photos
19 Aug.	Applied 100 kg/ha of muriate of potash using a hand spreader to all plots. Lumpy but still P responses present (Rowan Maddern).	Fertiliser
5 Sept.	Sprayed with 100 mL/ha urea ammonium nitrate sulphur and 125 mL/ha Lemat. The experiment looks ok and will need to measure in 1–2 weeks. Need to call Rob about grazing the back section. Photos were taken (Rowan Maddern).	Spraying Photos

Date	Notes	Action
16 Sept.	The experiment measured, both fresh and residual and 6 cuts taken. Look to be density response under the grass setting seed. Too late for grab samples, Rob has locked the paddock, and all species are setting seed. Rolled the fence up and will soil sample early next year. Photos were taken (Rowan Maddern).	DMY measurement Photos
2 Feb. 2012	Soil sampled all plots at 0–10 cm in the back section (fresh and residual). Subsurface sampled all nil-P and 25 kg/ha P plots from all reps at 10–20 and 20–30 cm. Pulled all logs and pegs out and packed up the site. Photos were taken (Rowan Maddern and Ryan Guthrie).	Soil sampling

9.3.4.2 Field experiment site-2

Table 9.15 Full experiment design (2009–2011).

Plot	Trt	Fertiliser	P kg/ha
1	9	Single superphosphate	25
2	3	Single superphosphate	5
3	5	Single superphosphate	10
4	2	Low water-soluble superphosphate	5
5	7	Single superphosphate	15
6	1	Nil-P	0
7	6	Low water-soluble superphosphate	15
8	4	Low water-soluble superphosphate	10
9	8	Low water-soluble superphosphate	25
10	1	Nil-P	0
11	2	Low water-soluble superphosphate	5
12	3	Single superphosphate	5
13	4	Low water-soluble superphosphate	10
14	5	Single superphosphate	10
15	6	Low water-soluble superphosphate	15
16	7	Single superphosphate	15
17	8	Low water-soluble superphosphate	25
18	9	Single superphosphate	25
19	2	Low water-soluble superphosphate	5
20	9	Single superphosphate	25
21	1	Nil-P	0
22	3	Single superphosphate	5
23	7	Single superphosphate	15
24	8	Low water-soluble superphosphate	25
25	4	Low water-soluble superphosphate	10
26	6	Low water-soluble superphosphate	15
27	5	Single superphosphate	10

Table 9.16 Visual observations (2009).

Date	Notes	Action
18 May	The experiment was seeded with clover and ryegrass using the combine by Matt Evans on Sunday, 17 May. The site was pegged (Rowan Maddern and Ryan Guthrie).	Seeding
19 May	The experiment was top dressed as per design and had 2.5 t/ha of lime applied. The site was sprayed using the motorbike with 250 mL/ha Telstar (Rowan Maddern and James Easton).	Fertiliser Spraying
22 June	The experiment is pest free with good grass coverage and some patches of clover. A Large amount of capeweed at about 5 cm in diameter. Site sprayed with 100 mL/ha Lemat and 600 mL/ha MCPA. No visual responses. Est. 1 t/ha dry matter yield and Matt Evans has seeded the paddock and locked it up. The fence still working (Rowan Maddern).	Spraying
23 July	Experiment plated at 30 plates per plot. Est. 1.8 t/ha dry matter yield. Scores were done, and the fence was disconnected because Matt has locked the paddock up. No signs of pest and cape weed have died off (Rowan Maddern and Ryan Guthrie).	DMY measurement
31 July	The experiment looks P responsive to 25 kg/ha of P in the third rep in both SSP and LWSSP. The front block has better growth than the second block. Grab samples were taken from plots, 1, 6, 9, 10, 17, 18, 20, 21 and 24. Photos were taken, and the experiment may need a 100 L/ha of urea ammonium nitrate and maybe potassium and sulphur (Rowan Maddern and James Easton).	Tissue sampling Photos
6 Aug.	Experiment plated at 30 plates per plot and 7 cuts taken. The site is 50% sub. Clover (Balansa) and grass. The fence was dropped, and the site will be grazed soon by Matt Evans, LWSSP looks about the same as the next lowest rate of SSP. Clover and grass look purple on the tips and has blotches in the middle of the clover leaf; there could be another problem, not nutrient related (Rowan Maddern and Ryan Guthrie).	DMY measurement Fencing
10 Aug.	Clover ravished by potassium deficiency – suggest 100 kg/ha muriate of potash be applied ASAP and 100 kg/ha NS41 to boost production and to try and draw out the P responses. Estimate about 1.2 to 1.8 t/ha dry matter yield – density a limiting factor. Plots uneven in their response – front of the trial responds best in the third and fourth reps. Good P responses nonetheless. Check soil test results down the profile (10–20 cm and 20–30 cm look like they should be the other way around (James Easton, CM, Brad Smith, AS).	
1 Sept.	Matt has the 40 cows and 40 calves in the paddock and will be in for a week. Talked to Brad Smith and he said	

Date	Notes	Action
	that P and S ratio are the same for the LWSSP so that the S rates will match up (Rowan Maddern).	
4 Sept.	The trial has been grazed and will need to be fenced up at the start of next week. Top dressed out the September fertiliser and est. 1.5 (t/ha) dry matter yield (Rowan Maddern and Ryan Guthrie).	Fertiliser
8 Sept.	The site was fenced up at the back section and 40 plates taken as the background 0.85 t/ha dry matter yield, photos taken (Rowan Maddern).	Photos
1 Oct.	30 plates taken from all plots and 6 cut's taken. Grab samples taken from all plots. Photos taken of all plots and it looks like SSP maybe ahead of LWSSP. Talked to Matt and maybe last measurement for the year and will have to look into letting set seed for next year (Rowan Maddern and Ryan Guthrie).	DMY measurement
6 Oct.	Pasture is quite vigorous and obviously benefitting from nitrogen, sulphur and potassium fertiliser top ups. Excellent responses to P and LWSSP look to be as effective as SSP. Cattle being moved out, so no new fencing required. Background plots need measuring individually before next assessment (James Easton, Ryan Guthrie, CM and Brad Smith).	
9 Oct.	Plated each of the background plots estimated dry matter yield ranging from 1.2 to 1.7 t/ha and took 6 calibration cuts. Rolled up the fence – cows now out of the paddock until after the season (James Easton and Ryan Guthrie).	DMY measurement
12 Oct.	Photos were taken of plots 13 and 14. Power pack picked up (Rowan Maddern and Ryan Guthrie).	Photos
21 Oct.	Experiment plated at 30 plates per plot and 7 cuts taken. Est. 2.5 t/ha dry matter yield and grab samples taken from every plot. Matt will graze the trial site over summer to remove the dry matter, and I will now let self-seed for next year. Photos were taken of every plot (Rowan Maddern).	DMY measurement Photos

Table 9.17 Visual observations (2010).

Date	Notes	Action
21 Jan.	Soil sampled taken from the nil-P, 25 LWSSP and 25 SSP kg/ha plots in all three rep. Sampled 10–20 cm and 20–30 cm in third rep of the same treatments. I have also sampled the paddock (Rowan Maddern).	Soil sampling
29 Mar.	The trial has top-dressed with 200 kg/ha urea and granular sulphate of ammonia 3:1 and 150 muriate of potash. The P fertiliser was spread by hand on both sections. The site had 50mm of rain 7 days before, and clover and ryegrass had germinated. Matt has pulled the cows out and so will not need to fence up for a while yet. Grass at half leaf, clover at cotyledon (Rowan Maddern and Ryan Guthrie).	Fertiliser
30 Mar.	Photos were taken (Rowan Maddern and Ryan Guthrie).	Photos
17 June	Soil sampled nil-P and 25 kg/ha SSP at 0–10 cm in the front block (Freshly applied). Lots of large capeweed and sprayed the site with 120 (L/ha) urea ammonium nitrate, 1.5 (L/ha) MCPA 500 and 100 mL/ha Lemat. The site has good soil moisture and Matt plans to move the cows in a week or two. Est. 1–1.5 t/ha dry matter yield. There was not much clover, and the site is very grassy. Photos were taken (Rowan Maddern).	Soil sampling Spraying Photos
7 July	The experiment measured all section (Aa-Bb) and leaf samples were taken from nil-P, 25 SSP and 25 LWSSP kg/ha plot in block A. Matt will move the cows in next week and then will fence up a section. Photos were taken (Rowan Maddern).	DMY measurement Photos
23 July	Site sprayed with 120 L/ha urea ammonium nitrate sulphur and 400 mL/ha Tiger X. Soil samples taken from nil-P, 25 LWSSP and 25 SSP kg/ha plots for Geoff. Large amounts of Capeweed and the background is between 0.5–2.0 t/ha dry matter yield. Have not fenced up the trial and will give the cows another week. The site does not look that good and may not be able to get anything out of it this year. I need a graze early in the season. Photos were taken (Rowan Maddern and Ryan Guthrie).	Spraying Fertiliser Photos
2 Aug.	Site back section was fenced up. Cows have done a good job grazing the site down. Est. 0.8 t/ha dry matter yield and plated the section at 30 plates. Photos were taken no sign of bugs (Rowan Maddern and Andreas Neuhaus).	DMY measurement Photos
30 Aug.	Soil samples taken from nil-P and high SSP/LWSSP plots for Geoff. Est. 1.0 (t/ha) dry matter yield and 150 kg/ha muriate of potash applied by hand to all plots (Rowan Maddern and Doug Hamilton).	Soil sampling Fertiliser
22 Sept.	100% ryegrass. Capeweed dead. Very dry. 28°C. Ryegrass at the milky dough. The trial is finished for this season. No responses (photos were taken) (Rowan Maddern and Ryan Guthrie).	
21 Oct.	Experiment have finished (Rowan Maddern).	Fencing

Table 9.18 Visual observations (2011–2012).

Date	Notes	Action
20 Jan.	Soil sampled all plots from front block 0–10 cm (54 plots), very site bear. Photos were taken. (RM) A = fresh fertilisers 2010, B = residual fertiliser 2010 (Rowan Maddern).	Soil sampling Photos
17 Mar.	Soil sampled (10–20) and (20–30) cm from nil and 25 kg/ha SSP/25 LWSSP plots. Site grazed well down and very dry. Photos were taken and Matt will re-sow the paddock just after first rainfall due to being grazed so hard. May need to spray out Kyk glass (Rowan Maddern).	Soil sampling
4 Apr.	Top dressed SSP/LWSSP by hand and then used cone top dresser to applied 150 kg/ha of muriate of potash and 150 kg/ha granular sulphate of ammonia. The site is very dry, and photos were taken. Matt will sow paddock around ANZAC day (Rowan Maddern, Andreas Neuhaus).	Fertiliser
19 May	Matt sowed the trial (Rowan Maddern).	Seeding
3 June	Sprayed out 100 mL/ha Lemat, Good soil moisture and the trial has not come up as well as the paddock. Matt has run the harrows over the site so it is a bit slow. Est. 0.3 t/ha dry matter yield and photos were taken (Rowan Maddern).	Spraying Photos
12 July	Viewed the trial site, the site had good soil moisture and is looking a lot better than last time. Clover and ryegrass have come up and spread out, but still a lot of bare spots. Est. 1.2–1.3 t/ha dry matter yield and will not be able to measure due to low growth. Matt is going to graze the paddock and will graze the site and set up for next measurement. Need to spray out urea ammonium nitrate post-grazing. Scores did on back residual block and photos were taken (Rowan Maddern and Ryan Guthrie).	Photos
1 Aug.	Sprayed out 100 L/ha urea ammonium nitrate using a motorbike. The site is grazed well and fenced up back section. About 0.6 t/ha Background dry matter yield. Site very wet and photos were taken (Rowan Maddern).	Spraying Fertiliser Photos
19 Aug.	Applied 100 kg/ha muriate of potash using hand spreader to all plots. No much growth but still looks good. Photos were taken (Rowan Maddern).	Fertiliser Photos
5 Sept.	Sprayed 100 L/ha urea ammonium nitrate sulphur and 125 mL/ha Lemat. Trial looks ok and more growth than a week ago. Will need to measure and grab in 1–2 weeks' time. Cows are in the paddock. Photos were taken (Rowan Maddern).	Spraying Fertiliser
16 Sept.	The experiment measured (6 cuts) and grab samples were taken (grass). Site composition is 80% grass, 10 sub clover and 10% other. The fresh site looks darker then residual, but there is no good visual different between the treatments. Must be 3.0 t/ha dry matter	DMY measurement Tissue sampling Photos

Date	Notes	Action
	yield in the section. Photos were taken and the fence moved to the front section. Good soil moisture and matt has had 40 mm for the last 5 days with more on the way this week (Rowan Maddern).	
12 Oct.	The site was measured and grab samples (70% clover, 30% grass) taken from both fresh and residual sections. Looks to be a slight phosphorus response and there is lots more clover in the residual section. Compression = 60% grass, 20% clover and 20% capeweed. The fence was shifted to the back section and photos taken. The background was plated but there 1.2 t/ha dry matter yield (Rowan Maddern and Ryan Guthrie).	DMY measurement Tissue sampling Photos
17 Oct.	Experiment sprayed with 120 L/ha urea ammonium nitrate sulphur (Rowan Maddern).	Spraying
5 Nov.	Measured trial by eye because plots are too far gone and setting seed, so no grab samples possible. Look to be still P response of about 0.5 t/ha from nil-P to higher plots. Photos were taken and 6 cuts taken to calibrate visual scores. Fence rolled up (Rowan Maddern and Ryan Guthrie).	Measurement Fencing
7 Nov.	Took a quad cut out of every plot (Fresh and Residual) in the rear section and will get the dry matter production data from the lab. I will then run the samples through for analysis to see if there is any different in P uptake at this late stage of the growth cycle. I will soil sample the site early next year as an experiment is finished for the year (Rowan Maddern).	DMY measurement
7 Feb. 2012	Experiment soil sampled from both fresh and residual sections (all plots) on the front block at 0–10 cm. Photos were taken (Rowan Maddern).	Soil sampling Photos
8 Feb. 2012	All control and 25 kg/ha of phosphorus plots sampled at 10–20 and 20–30 cm in the fresh front section. Post pulled out and all pegs removed as an experiment is finished (Rowan Maddern, Ryan Guthrie).	Soil sampling Fencing

9.3.4.3 Weather and climate data

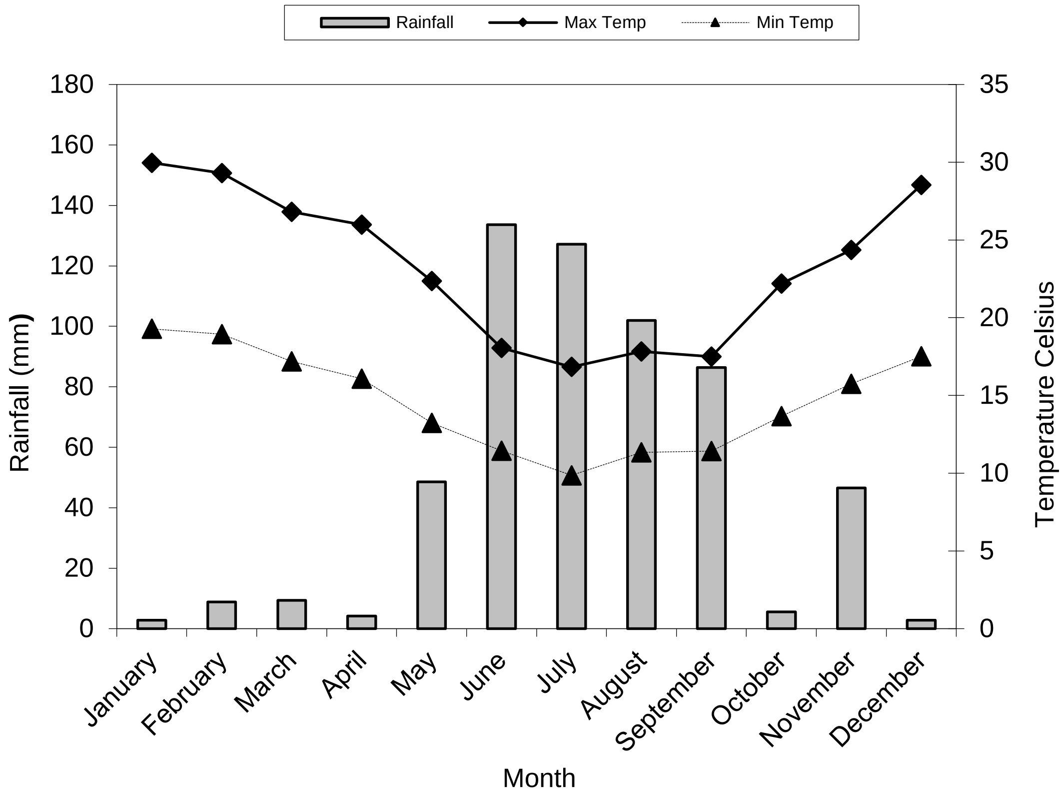

Figure 9.10 Mandurah climate for 2009.

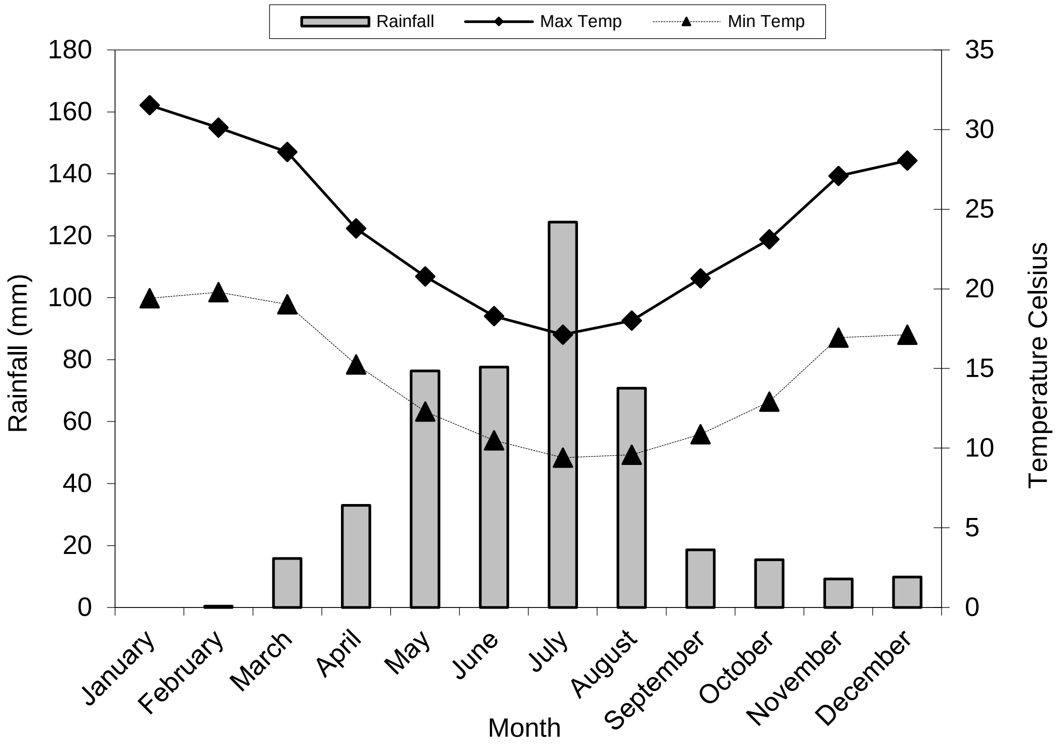

Figure 9.11 Mandurah climate for 2010.

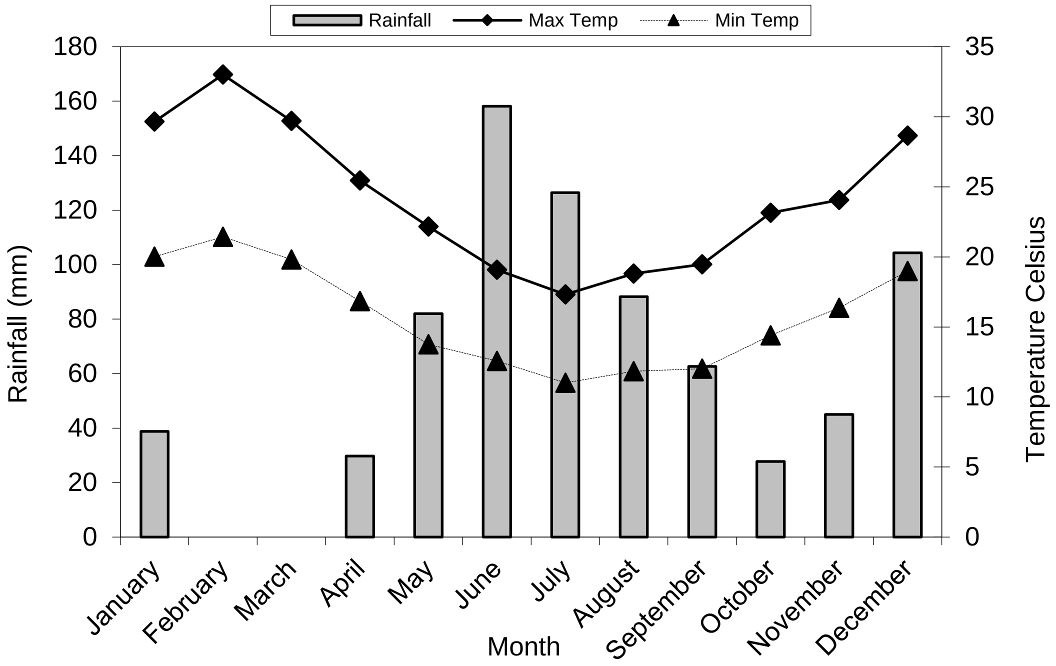

Figure 9.12 Mandurah climate for 2011.

9.3.4.5 Example of the statistical analyses

ANOVA analysis of dry matter grams (glasshouse experiment 1)

Analysis of an unbalanced design using GenStat regression

Variate: DM_g

Accumulated analysis of variance

Change	d.f.	s.s.	m.s.	v.r.	F pr.
+ Run	5	68.6185	13.7237	93.99	< .001
+ Run.Tank	12	23.6207	1.9684	13.48	< .001
+ Species	1	0.0007	0.0007	0.00	0.945
+ Fert	0	0.0000	*		
+ Species.Fert	5	2.0056	0.4011	2.75	0.024
Residual	84	12.2651	0.1460		
Total	**107**	**106.5106**	**0.9954**		

Predictions from regression model

The standard errors are appropriate for interpretation of the predictions as summaries of the data rather than as forecasts of new observations.

Response variate: DM_g

Species	Prediction	se
Clover	1.882	0.05200
Ryegrass	1.877	0.05200

Least significant difference (at 5.0%) for predicted means 0.1462

Regression analysis of total dry matter yield

REML variance components analysis

Response variate: Total_Prod

Fixed model: Constant + FERTILISER + SOIL + SPECIES + FERTILISER.SOIL + FERTILISER.SPECIES + SOIL.SPECIES + FERTILISER.SOIL.SPECIES

Random model: BENCH.SECTION.ROW

Number of units: 84

BENCH.SECTION.ROW used as residual term with covariance structure as below.

Sparse algorithm with AI optimisation

Units with missing data values included

Covariance structures defined for random model

Covariance structures defined within terms:

Term	Factor	Model	Order	No. rows
BENCH.SECTION.ROW	BENCH	Identity	1	3
	SECTION	Auto-regressive	1	4
	ROW	Auto-regressive	1	7

Residual variance model

Term	Factor	Model (order)	Parameter	Estimate	s.e.
BENCH.SECTION.ROW		Sigma2	0.428	0.0931	
	BENCH	Identity	-	-	-
	SECTION	AR(1)	phi_1	0.05318	0.18285
	ROW	AR(1)	phi_1	0.4741	0.1379

Tests for fixed effects

Sequentially adding terms to fixed model

Fixed term	Wald statistic	n.d.f.	F statistic	d.d.f.	F pr
FERTILISER	12.47	2	6.22	36.4	0.005
SOIL	11.58	2	5.79	37.7	0.006
SPECIES	689.22	2	344.55	41.6	< 0.001
FERTILISER.SOIL	1.27	4	0.32	40.3	0.865
FERTILISER.SPECIES	30.43	4	7.59	40.7	< 0.001
SOIL.SPECIES	33.16	4	8.27	40.0	< 0.001
FERTILISER.SOIL.SPECIES	11.77	8	1.46	38.0	0.203

Dropping individual terms from full fixed model

Fixed term	Wald statistic	n.d.f.	F statistic	d.d.f.	F pr
FERTILISER.SOIL.SPECIES	11.77	8	1.46	38.0	0.203

Message: Denominator degrees of freedom for approximate F-tests are calculated using algebraic derivatives ignoring fixed/boundary/singular variance parameters.