

MANAGING PHOSPHORUS IN INTENSIVE PASTURE SOILS TO IMPROVE THE LONG-TERM ENVIRONMENTAL SUSTAINABILITY OF THE DAIRY INDUSTRY

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DEDICATION

In loving memory of my Father, who was always proud, and encouraged me to do my best; *“Good on you kid, do all you can do, get all the knowledge you can get”*. It was after his passing that I decided to undertake my PhD.

I also dedicate this thesis to my Mother, whom I greatly respect and love. I look forward to writing your entertaining and diverse life story with you.

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PREAMBLE

Throughout this thesis, the term phosphorus, or its chemical symbol 'P', will be used. With respect to P fertiliser, it is acknowledged that the correct term is phosphate fertilisers, however, the term phosphate will only be used where specific definition is required. However, before we get too bogged down with the details concerning P in pasture soils, let's get to know the element a little.

The word phosphorus is derived from the Greek words *phos* and *phorus*, which mean 'light' and 'bringing', respectively. Phosphate was the thirteenth element to be discovered – and interestingly it hasn't had a completely pleasant impact on the world. Ironically, during the Battle of Hamburg in World War II, thousands of P laden fire bombs engulfed the city, where P was first discovered by an alchemist in 1669. Phosphate was first sold as a medical treatment in the seventeenth century to increase intelligence, and was still available over the counter in the 1950s; however, this perceived benefit encouraged overdosing and in some cases led to death (Emsley, 2000). Perhaps the agriculture industry of today can learn from experiences of the past.

ABSTRACT

By definition, there is little or no pasture production benefit of plant available soil phosphorus (P) concentrations above agronomic optimum. Soil P concentrations above the agronomic optimum can result in unnecessarily elevated P concentrations in runoff that can adversely impact on water bodies. I hypothesised that a reduction in these excessive P concentrations in pasture soils may be achieved through applying fertiliser P at rates that are less than those required to maintain soil P concentrations. This thesis considered this hypothesis by utilising six established field sites which represented the broad range of soils used for pasture production in south eastern Australia (Burkitt *et al.*, 2001; Burkitt *et al.*, 2006). The soils at the sites encompassed a wide range of P buffering indices (PBI) (from 6–519) and textures (sand to clay loam). At each site a replicated trial consisting of four initial soil P (P_{init}) concentrations combined with four on-going P fertiliser rates (P_{fert}) had been previously established, and soil samples taken from these trials formed the basis for much of the work presented in this thesis.

The first experimental chapter (Chapter 2) reports on the changes in extractable P of these field soils which were sampled (0-10 cm) once every six months (biannually) for up to four and a half years. Phosphorus extractable in calcium chloride ($CaCl_2$ -P) was monitored using annual samples of the two lowest and the highest P_{init} concentrations receiving the two lowest and the highest on-going P_{fert} rates. Olsen- and Colwell-extractable P concentrations were monitored biannually for all sixteen treatments. Excluding a soil with an extremely low PBI where soil P concentrations could not be increased, the study revealed decreases to be larger the greater the P_{init} concentration, and the smaller the on-going rate of P_{fert} . The influence of P_{fert} on decreases in extractable soil P was not as large as that of P_{init} concentration. The relative decrease in the more readily available $CaCl_2$ -P (-57%) was greater than relative decreases in the agronomic measures, Olsen-P (-25%) and Colwell-P (-12%). When P_{fert} was withheld, soil P concentrations initially well above agronomic optimum remained above this level. This study advances the knowledge of P decline characteristics and will aid land managers in understanding likely changes in soil P concentrations when P fertiliser inputs are reduced.

The second experimental chapter (Chapter 3) reports the development of a model to assist policy makers and land managers in setting realistic timeframes to return soils with excessive P to agronomic and/or environmental optimum. The model utilised the original field study's (Chapter 2) $CaCl_2$ -P, Olsen-P and Colwell-P dataset. The model assumed and confirmed the suitability of an exponential decay function and predicted the final P concentration for $CaCl_2$ -P, Olsen-P or Colwell-P as: Final P concentration = (previously measured P concentration + $e \times P$ fertiliser applied) $\exp(-d \times \text{years since P applied})$; where e is the increase in soil P for each unit of applied P and d is the decay constant representing how quickly the soil P moved from the labile to unavailable P pools. Using parameters derived across all the soils, where P exports ranged from 2.9 and 12.3 kg P/ha.yr, the model predicts it would take approximately 14 years (ranging from 11 to 20 years) for Olsen-P concentrations of between 34 and 44 mg/kg to decrease to an agronomic optimum of 17 mg/kg. An initial Olsen-P concentration of between 55 and 96 mg/kg would take approximately 32 years (ranging from 26 to 49 years). Using soil specific parameters, the model also identified that some soils, i.e. those with high PBI, could

be maintained at agronomic optimum P concentrations without the risk of environmental loss being above the specified $\text{CaCl}_2\text{-P}$ threshold of 0.25 mg/kg (0.05 mg/L). In contrast, soils with low P sorption capacity exceeded the environmental threshold even when soil P concentrations were below agronomic optimum i.e. Olsen-P 14-17 mg/kg. Despite soil P decreases varying according to soil, a soil term was not incorporated into the model as there were only six soils studied. Further work incorporating more soils and various P exports is required to examine the influence of soil properties such as P sorption, and P export, on decreases in soil P.

Chapter 4 reports on an investigation of the changes in further soil P pools as extractable P concentrations of selected treatments of Chapter 2 decreased. These treatments included the two lowest and the highest P_{init} concentrations which received no on-going P_{fert} treatment. This research revealed that the majority of the P was not being exported or sorbed, but inorganic P (P_i) was being converted to organic P (P_o). A longer period of monitoring is required to examine if the P_o concentration will stabilise once a maximum P_o concentration is approached. Relationships between the various P measures allowed us to calculate a degree of P sorption saturation (DPSS) for these soils. Degree of P sorption saturation was relatively low for the two lowest PBI soils when compared to higher PBI soils, despite $\text{CaCl}_2\text{-P}$ concentrations being some of the largest reported in the literature. Further correlation of DPSS with P losses from Australian soils is required as we suggest that the thresholds will vary for soils with extreme P sorption capacities. Alternative methods of calculating DPSS, using Australian measures such as P sorbed after the addition of 1000 mg P/kg, as measured as part of the PBI method, and Colwell-P, without the requirement of an alpha value, were proposed.

Chapter 5 reports the findings of an incubation study and the longer-term effect of drying and rewetting soils. It was found that extremely low PBI soils with high organic matter (OM) contents may be at high risk of P loss to the surrounding environment. Chapter 5 showed that drying and rewetting the soils with the lowest PBI produced large increases in $\text{CaCl}_2\text{-P}$ and Olsen-P, hypothesised to be of microbial and OM origin. Thus, irrespective of fertiliser management, there are large risks of P loss from such soils, even when Olsen-P concentrations are below agronomic optimum. In comparison, P released from soils of higher PBI did not result in large increases in $\text{CaCl}_2\text{-P}$, which remained below the threshold of environmental concern, probably due to chemical sorption.

The large potential for P loss from soils of extremely low PBI was further highlighted in the final experimental chapter (Chapter 6). Chapter 6 compared extractable soil P concentrations of the lowest and highest PBI soils to a depth of 100 cm. It was revealed that soil with an extremely low PBI was susceptible to large P losses, with the majority of applied fertiliser P i.e. 81% (406 kg P/ha) not recovered in this deep sampling zone. Such a large potential loss of applied P brings into question whether such soils should be used for agricultural purposes, especially if soluble P fertiliser is applied, unless the soil's ability to sorb P is firstly increased through the application of a suitable amendment.

Until preferred soil P extractions and thresholds have been accepted for determining the risk of P loss according to soil P concentration and buffering capacity, the depletion of soil P concentrations of intensively

grazed pastures to agronomic optimum must be encouraged. Only once agronomic optimum soil P concentrations are reached should the appropriate maintenance P fertiliser application, to account for soil sorption and P exported in produce, be supplied. However, the currently defined agronomic optimum i.e. Colwell-P of 23 mg/kg for PBI <15, may be too high for extremely low PBI soils. Phosphorus fertiliser management for low PBI soils requires more precision than higher PBI soils to limit environmental loss of P. Indeed, intensive grazing of extremely low PBI soils is questionable until their PBI's are increased through application of amendments.

GENERAL INTRODUCTION

Pasture-based Australasian dairy production places great emphasis on soil P concentration. Since pasture is the cheapest feed source, fertiliser P is typically used to achieve and maintain soil P concentrations at or above that required for optimum pasture production. However, soil P concentrations above agronomic optimum (excessive soil P concentrations) are common in Australasian intensively grazed pasture soils. These excessive soil P concentrations are the result of P imports in fertilisers, effluent, and livestock fodder, exceeding removal in farm produce, runoff, and leaching. An Australia-wide study by Gourley *et al.*, (2010) found that 80% of 1773 pasture paddocks sampled from 37 conventional dairy farms had Olsen-P concentrations above agronomic optimum (14-17 mg/kg), with 50% of these paddocks having concentrations one and a half times, and 20% at least three times the agronomic optimum.

Excessive soil P concentrations are not only an unnecessary economic expense and use of a finite resource of raw P (Cordell *et al.*, 2009); they also pose a risk to the surrounding waters. Indeed, surface P runoff from intensively managed Australian dairy pasture soils has been reported to contain total-P concentrations in the range of 0.9–35.0 mg/L (Nash *et al.*, 2000; Dougherty *et al.*, 2008; Burkitt *et al.*, 2010b). It has generally been accepted that the more P there is in a soil, the greater is the risk of environmental loss (Sharples and Rekolainen, 1997; Burkitt *et al.*, 2010b).

Reducing excessive soil P concentrations through reducing or withholding P fertiliser could potentially reduce P losses to the environment. However, little is known of the decrease in so-called environmental and agronomic P concentrations when P fertiliser is reduced or withheld, especially for a range of initial P concentrations (P_{init}), and soil P sorption properties, representative of intensive pasture grazing systems.

It was the objective of this thesis to;

- 1) describe the decrease in soil P concentrations of a range of PBI pasture soils, which each contained a range of P_{init} concentrations, and received a range of on-going P fertiliser (P_{fert}) rates,
- 2) develop a model to predict the final environmental and agronomic soil P concentrations according to P_{init} concentration, rate of on-going P fertiliser, if supplied, and time since P fertiliser application had occurred,
- 3) quantify the processes influencing the changes in environmental and agronomic P concentrations when P fertiliser is withheld, particularly the degree of P sorption saturation (DPSS),
- 4) assess the magnitude and duration of changes in P pools after drying and rewetting (DRW) soils in order to understand how PBI affects the potential of DRW cycles to supply bio-available P pools, and
- 5) assess the influence of soil texture and PBI on downward P movement by comparing P recovery from the surface 100 cm of two contrasting soils.

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**DECREASE IN SOIL PHOSPHORUS CONCENTRATIONS WHEN PHOSPHORUS
FERTILISER APPLICATION IS REDUCED: A LITERATURE REVIEW**

INTRODUCTION

Australasian dairy systems rely heavily on the use of intensively grazed pastures as the main source of feed for cattle. As a result, great emphasis has been placed on building soil P concentrations to agronomic optimum through application of P fertiliser when soils are either naturally low in P, or where P concentrations have been depleted through previous exports in agricultural products such as milk and fodder.

Phosphorus fertiliser is normally applied to the surface of established pasture soils as inorganic granular formulations. When P fertiliser is applied, the dissolved P can either remain in solution where it can be taken up by plants and micro-organisms, become weakly adsorbed, precipitate as initial reaction products, become strongly absorbed, or lost from the soil via leaching and runoff – potentially entering surrounding water bodies. Phosphorus is often a limiting nutrient for algal growth (Sharpley *et al.*, 1987; Leinweber *et al.*, 2002). Whilst most algal blooms reduce water quality and aesthetic appearance, they can also produce harmful toxins. Algal blooms associated with P loss from intensively grazed pastures may also have an adverse impact on the dairy industry, due to increasing demand for ‘clean and green’ products from consumers (Williams and Hook, 1998) and an expectation from the community that industries will use best practice management and have a minimal impact on the environment. In addition, excessive soil P concentrations are an inefficient use of a finite resource (Cordell *et al.*, 2009) if the applied P is not eventually utilised by the plant but is lost from the soil/plant system.

The link between increasing soil P concentrations and the concentration of P in surface runoff is well established (Sharpley and Kleinman, 2003; Vadas *et al.*, 2005; Burkitt *et al.*, 2010b). Thus, accumulation of P in soil in excess of that required for optimum pasture production further increases the risk of P loss to surrounding waters. While there are water quality targets in regard to P concentrations, there currently are not any thresholds for environmental i.e. CaCl_2 , or agronomic i.e. Olsen or Colwell, soil P extractions in Australia. Soil CaCl_2 -P concentrations above 0.25 mg/kg (0.05 mg/L) are generally used as an indicator for runoff studies, above which P concentrations are considered to negatively influence water quality. Quantities of P imported in fertiliser, concentrates, and fodder, exceeding P exported in fodder and animal products has resulted in many Australasian dairy pasture soils containing P far in excess of agronomic requirements (Hedley *et al.*, 2002; Burkitt and Coad, 2006; Gourley *et al.*, 2010). Excessive soil P concentrations also occur in intensively managed soils in other parts of the world (Sims *et al.*, 1998; Pautler and Sims, 2000).

There are a number of methods available to amend excessive soil P concentrations such as applying P sorbing amendments (Summers *et al.*, 1996; Murphy and Stevens, 2010) and de-stratifying the surface soils (Dougherty *et al.*, 2006), which are generally used if rapid reductions in soil P concentrations are required. However, the most obvious solution, and one that the land manager is most likely to adopt due to neutral implementation cost, is reducing or withholding P fertiliser applications. Withholding P fertiliser application has a twofold impact; 1) it reduces the risk of incidental P loss from P fertiliser application (Burkitt *et al.*, 2011), and 2) it slowly decreases soil P concentrations and, thus, reduces the risk of P loss. However, further knowledge is required of decreases in extractable soil P concentrations when P fertiliser is reduced or withheld.

This review of the literature summarises current knowledge regarding the relationship between agronomic and environmental extractable soil P concentrations, and their decrease when P fertiliser application is omitted, or is at a rate below that required to maintain an excessive extractable soil P concentration.

PHOSPHORUS FERTILISER USE AND MANAGEMENT

In Australia, 45% of fertiliser sold in 2011/2012 was superphosphate, worth \$1.8 billion, with the majority of this fertiliser applied to pastures (Richardson, 2012). Avoiding environmental P losses requires consideration of not just soil P concentration, but also P fertiliser management. The fertiliser type and solubility (Withers *et al.*, 2001), and the rate, placement and timing of application can have a major effect on the forms and amounts of P lost in runoff (Romkens and Nelson, 1974; Eghball and Gilley, 2001; Burkitt *et al.*, 2011).

Phosphorus fertiliser rate and blend should be targeted according to the soil extractable P concentration of individual paddocks. Once optimum agronomic extractable P concentrations are achieved, P fertiliser should be applied at rates sufficient to only replace exports in farm product and soil reactions, in order to maintain P fertility. This is referred to as a 'maintenance' application rate. Although progressive Australian dairy managers use soil analysis and nutrient budgets to more precisely apply P fertiliser to maintain concentrations at agronomic optimum, nutrient budgets are not compulsory, and are, thus, not as prevalent as they should be. Some land managers are reluctant to change their fertiliser and soil P management practices due to the belief that it may compromise pasture production. As a result, some land managers continue applying 'insurance' P fertiliser in order to maintain or increase their already excessive extractable soil P concentrations. They are of the view that they will not be able to afford the lost production if they reduce fertiliser P inputs, even if they can't really afford the fertiliser itself (Nicon Rural Services, 2010). In part, this 'fear of loss' mindset may be due to a lack of awareness regarding the diminishing pasture response once agronomic optimum extractable soil P concentration is surpassed, but also the contribution agricultural management can make to eutrophication and water quality decline. If a land manager is convinced to trial lower fertiliser P inputs on selected areas which are excessively concentrated in P, any impact on pasture production may become evident. However, the impact of reducing soil P concentrations and the risk of P loss to the surrounding environment is more difficult to demonstrate due to the multiple sources of nutrients entering water ways and the long lag times for improving water quality.

ENVIRONMENTAL IMPACT

It is important that land managers recognise that a very small amount of P compared to the amount applied on a farm scale can have drastic effects on water quality, often at a considerable distance from the point of application. Although effort has been made to reduce point-sources (e.g. effluent disposal in waterways), the contribution of non-point sources such as surface and subsurface P losses (Sharpley *et al.*, 1994; Parry, 1998) has become increasingly recognised. Several studies have demonstrated that surface P losses from pasture-based industries pose a substantial risk to water quality (Austin *et al.*, 1996; Nash and Murdoch, 1997; Fleming and Cox, 2001; Schärer *et al.*, 2007). Monaghan (2008) reported that for modern non-irrigated dairy farms, P

loss ranged from 0.3 to 5.0 kg P/ha.yr. This represented 1-10% of farm P inputs via fertiliser or feed, or much less than 1% of the total mass of P resident in the soil profile (Monaghan, 2008). Measured surface runoff losses from a non-irrigated, intensively grazed dairy catchment in north-west Tasmania were 10.0 kg P/ha.yr (Holz, 2010), and modelled losses were 11.1 kg P/ha.yr in a neighbouring catchment (Broad and Corkrey, 2011).

Discharge of P from agriculture is recognised as being widespread in Europe and is a target for tighter control measures (Parry, 1998; European Parliament and Council, 2000). Regulations in the Netherlands, for example, require calculation of nutrient balances in order to assess the risk of nutrient loss from a farm (Neeteson *et al.*, 2001). Land managers who cannot meet these targets are subject to the 'polluter pays principle', where the operator is financially liable for the surplus P and remedying the damage. However, maintenance of a P balance may still result in loss of P from an already highly concentrated soil. Although there has been a decline in P fertiliser use and in the number of soils excessively concentrated with P since the introduction of the Nitrates Directive policies in Ireland in 2006 (SI 378, 2006), some soils are still excessively concentrated with P due to past over application of P fertilisers and manures (Wall *et al.*, 2012).

Public awareness of the negative effects of agriculture on water quality has made it an area for concern for the Australasian dairy industry if it is to be seen as environmentally and sociably sustainable (Williams and Hook, 1998). Mitigation strategies for P loss implemented by Australian land managers will need to have minimal trade-offs between the environment and farm income in order to be adopted, as financial support such as that available in the United States of America and Europe is unlikely to be provided. To limit their environmental impact, Australian dairy managers will be more likely to voluntarily adopt practices involving management changes which are easy to evaluate (Pannell *et al.*, 2006), while maintaining long-term productivity, rather than those which require time or financial input.

PHOSPHORUS CYCLE UNDER INTENSIVELY GRAZED PASTURE

Phosphorus transformations and mobility in the soil-plant system are controlled by a combination of biological, chemical, and physical processes (Frossard *et al.*, 2000). Soil solution is the primary source of P for plant and micro-organism uptake (Williams, 1974), mostly as inorganic (Pi) orthophosphate (HPO_4^{2-} , H_2PO_4^-). Phosphorus removed from the soil solution is replenished by P released from Pi and organic (Po) forms associated with the solid phase (Condrón *et al.*, 2005). Phosphorus can be lost from the soil-plant system in animal products, transfer in excreta, absorption into the soil matrix and precipitation of sparingly soluble products, and as particulate and dissolved P in surface and subsurface runoff and leaching. Phosphorus is added to the soil system through weathering of parent material, the addition of P fertiliser, decaying plant matter, and animal excreta.

Sorption-desorption and precipitation-dissolution

The processes involved in adsorption–desorption and precipitation–dissolution of P_i have been studied extensively and are well understood (Frossard *et al.*, 1995).

Direct physical and chemical adsorption of P onto the surface of soil particles is reversible (desorbable) and is associated with what are arbitrarily referred to as ‘rapid reactions’ (Sanchez and Uehara, 1980). Most sorbed P in acidic and neutral soils is associated with amorphous hydrous oxides of aluminium (Al) and iron (Fe) (Condon and Goh, 1989; Burkitt *et al.*, 2002b), which are usually associated with the surface of clay and organic matter (Sample *et al.*, 1980). In alkaline soils, calcium carbonate ($CaCO_3$) is responsible for sorbing P from the soil solution (Sample *et al.*, 1980; McDowell *et al.*, 2003). However, soil pH has been reported to have a variable effect on P sorption, depending to soil type (Murphy, 2007; Murphy and Stevens, 2010).

Initial rapid sorption usually takes 24 to 48 hours to reach equilibrium, but may only take between 1 and 3 hours (Agbenin and Tiessen, 1995). Up to 75% of added soluble P fertiliser can be sorbed in 30 minutes by soils of high P sorption capacity and 12 hours for soils of low sorption capacity (Agbenin and Tiessen, 1995), and the sorbed P is usually in the labile form (Barber, 1995). Labile P is P which is in equilibrium with, and replenishes, the soil solution, through processes such as desorption and decomposition (Holford, 1997). Due to these rapid reactions between P fertiliser and soil, study of changes in extractable P concentrations may be comparable for soils where P concentrations were built-up through long-term, i.e. over a number of years, or short-term, i.e. within 12 months, P fertiliser application.

The majority of total P (P_t) is non-labile, considered to not be directly plant available since it is poorly soluble e.g. Po resistant to mineralisation, or precipitated P. Long-term P absorption or diffusion into the soil mineral structure (Barrow, 1974b; Barrow, 1983b) and nucleation-controlled precipitation of P reaction products from fertiliser, are ‘slow’ and almost irreversible (Brady, 1990; Leeper and Uren, 1993). An example is diffusion of P into microcrystalline Al and Fe oxides (Barrow, 1983b). The slow reaction continues for a long period, at a decreasing rate, and does not reach an end point or equilibrium (Barrow, 1974b; Bhat and Nye, 1974; Barber, 1995). Due to the long reaction time, the slow P sorption reaction could be considered more important than the initial rapid reaction in controlling soil P availability and any residual effect of added fertiliser P. Soil P concentrations built-up over a period of time would be subject to these slow P reactions, as well as P removal through animal and plant products, and environmental loss, for a longer period than soil P concentrations achieved over a short period of time. Indeed, slightly more P may be required to replace that lost through sorption reactions in this case, compared to a single large quantity of P fertiliser applied to achieve the same extractable soil P concentration. However, slow reactions have been reported to be independent of the amount of P fertiliser applied (Barrow, 1987). Thus, long-term decreases in extractable soil P concentrations may be similar, irrespective of whether the initial soil P concentration was built-up over a short or long period. Indeed, Barrow *et al.*, (1998) assumed the efficiency of P fertiliser applied to eight soils several years after their initial single application of P, which ranged from ~200 to 900 kg/ha depending on soil type, to be similar to soil which received a similar quantity of P over a number of years.

Sorption reactions account for the greatest immobilisation of P fertiliser (5-30 kg/ha.yr) (Cayley and Kearney, 1999; Gourley *et al.*, 2001) and influence the amount of P fertiliser required to increase, maintain or decrease extractable P concentrations (Barrow, 1973). A soil's P buffering capacity is a property that influences the relationship between sorbed P (P quantity) and P concentration in the soil solution (P intensity) (Holford, 1977). A soil's P buffering capacity is a function of the number and energy of P sorption sites. When a soil of low P buffering capacity is treated with a high rate of P fertiliser, the concentration of P in the soil solution will be high in comparison to that of a high buffering soil treated with the same rate of P fertiliser (Allen and Jeffery, 1990). This is because the bonding energy for P decreases as sorption saturation increases (Ryden *et al.*, 1977). Hence, soils with high P buffering tend to have a lower soil solution concentration, and negligible losses of P to water when compared to soils with low P buffering. Australian dairy farms are typically located on soils with low to moderate P buffer capacity [i.e. P buffering index (PBI) of 50–200] (Gourley, *pers. comm.*). Phosphorus buffering index is used in Australia as an index of a soil's P buffering capacity. Dougherty *et al.*, (2011a) reported that applying P to low PBI soils will result in relatively large incidental fertiliser effects and relatively large residual effects at the relevant half life when compared to soils with high PBIs.

Immobilisation-mineralisation

Immobilisation and mineralisation are processes that are largely influenced by the physical and chemical properties of the soil, as well as the nature of the micro-organisms present (Larsen, 1967; Dalal, 1977), and occur concurrently.

In addition to sorption, immobilisation includes the biological conversion of P_i to P_o in the soil via two major pathways. Firstly, removal of P_i from the soil solution can occur during microbial growth. Some of this microbial P is subsequently released in detritus following cell death and lysis (Alexander, 1977). Secondly, P_i removed from the soil by plant uptake is returned as P_o in litter, root debris, animal excreta and manure.

Inorganic P can be released through mineralisation of P_o derived from plant residues, animal excreta, soil fauna and micro-organisms, and is generally a slow process. Between 30 and 65% of total P in soil is in the organic form, with soils high in organic matter containing up to 90% of their P as P_o (Harrison, 1987). Barber (1995) suggested that the rate of P_o mineralisation is influenced by environmental conditions such as temperature and moisture content, soil texture, and phosphatase production.

EXTRACTABLE SOIL P CONCENTRATION AND P LOSS

Of particular importance to dairy pasture soils is stratification or the accumulation of P at the soil surface (Dougherty *et al.*, 2006). This is due to fertilisers being applied to the surface of Australasian pastures soils, which are rarely cultivated. It is the soil surface that first interacts with rainfall and irrigation (Eckert, 1985; Haygarth and Jarvis, 1999), which can lead to P loss in runoff (Sharpley *et al.*, 2000). Several studies of P export in runoff from Australian dairy pastures have demonstrated the potential for substantial risk to water quality (Austin *et al.*, 1996; Nash and Halliwell, 1999; Fleming and Cox, 2001; Dougherty, 2006; Schärer *et al.*, 2007; Burkitt *et al.*, 2010b).

The loss of P by surface runoff, and leaching below the root zone, increases as extractable soil P concentrations increase (Romkens and Nelson, 1974; Heckrath *et al.*, 1995; Sims *et al.*, 1998; Pote *et al.*, 1999; Hesketh and Brookes, 2000; Vadas *et al.*, 2005; Burkitt *et al.*, 2010b). Numerous relationships have been reported between so-called environmental measures of surface soil P, e.g. water extractable-P (WEP) and CaCl_2 -P, and dissolved reactive P or total-P concentrations of surface runoff (McDowell and Sharpley, 2001; Burkitt *et al.*, 2010b). In addition, relationships between environmental and agronomic P measures have been reported (McDowell and Sharpley, 2001; McDowell *et al.*, 2001a; Moody, 2011).

Agronomic soil P concentrations may be used as indicators of P loss risk. Vadas *et al.*, (2005) suggested that a single linear slope coefficient was justified for modeling extractable soil P concentration and P in runoff across a wide range of soils, although extreme soils with very high or very low clay contents may require different coefficients. This is because soils with low P sorption capacities would have less sorption sites than soils of higher P sorption capacities. These soils of lower P sorption capacity would be more prone to environmental loss due to P being held in low energy sorption sites, due to high energy sites already being saturated (Holford and Mattingly, 1976). In contrast to Vadas *et al.*, (2005), after reviewing the literature, Sibbesen and Sharpley (1997) and Koopmans *et al.*, (2002) concluded that across a wide range of extractable soil P concentrations, linear relationships between extractable soil P and P in runoff may become nonlinear. Indeed, Dougherty *et al.* (2011b) reported that a curvilinear relationship between Colwell-P and runoff P for the surface 1 cm of a number of individual soils could be explained by the P buffering capacity of the soils.

Identification of change-points beyond which there is a disproportionate increase in P loss has been reported for some soils (Hesketh and Brookes, 2000; Hooda *et al.*, 2000; McDowell and Sharpley, 2001). However, these change-points have been reported to be soil specific – according to P sorption/desorption properties – and to vary with management such as soil pH (McDowell *et al.*, 2001a). This suggests that the change-point approach may not be suitable for assessing the environmental loss risk across a range of soils. Vadas *et al.*, (2005) suggested that an indication of a soil's P sorption saturation i.e. the degree of P sorption saturation (DPSS), may provide a more universal prediction of P loss than agronomic or environmental P measures alone. Dougherty *et al.* (2011b) and Moody (2011) suggested measurement of soil PBI would be useful in this regard, in combination with a measure such as Colwell-P.

The DPSS method incorporates a measure of sorbed P and a measure of the total soil P retention capacity. Nonlinear (Lookman *et al.*, 1995; Koopmans *et al.*, 2001) and linear (Sharpley, 1995; Paulter and Sims, 2000) relationships have been reported between DPSS and WEP. Since P sorption is nonlinear, these reported linear relationships may be due to there not being a wide enough range in extractable soil P concentrations (Koopmans *et al.*, 2002). Beauchemin *et al.*, (1996) suggested that the critical DPSS threshold, after which the risk of P loss to the surrounding environment is above the environmental threshold, will vary with land use, soil physical and chemical properties, and surface water quality standards.

Similar to DPSS, McDowell and Condron (2004) calculated a quotient between P sorption index (PSI), or P retention (PR) (New Zealand measure of P sorption), and soil Olsen-P concentrations (i.e. Olsen-P/PSI). Moody (2011) reported that the index of Colwell-P/PBI was highly correlated with $\text{CaCl}_2\text{-P}$ ($r = 0.925$, $P < 0.001$) for a range of soils sampled to 10 cm. Preliminary results suggested that quotients of a soil P measure and a measure of P sorption capacity could be useful for describing the environmental risk, while removing the often curvilinear and soil specific relationship between WEP or $\text{CaCl}_2\text{-P}$, and agronomic, soil P concentrations. Although the DPSS and quotient approaches are improvements over a measure of soil P concentration alone, they do not account for the risk of P transport from the field and should be used in conjunction with an estimate of runoff or leaching potential such as landscape characteristics and land management.

Knowledge of the limitations of extractable soil P is important when regulatory programs are being developed. Until the influence of sorption capacity on P loss in relation to extractable soil P concentration is thoroughly defined, a blanket threshold for agronomic soil P, across a range of soils, may be inappropriate as a method to limit environmental P loss. There is a risk that some soils may still lose P at such a threshold. For example, extremely low P sorbing soils with a low ability to retain P may have Olsen-P concentrations which are below a given agronomic threshold, but their respective $\text{CaCl}_2\text{-P}$ concentrations may be high since the majority of their P is held in the readily available form. Indeed, there have been contrasting reports of thresholds for agronomic measures above which unacceptable P losses to the surrounding environment are likely to occur. For example, Hesketh and Brookes (2000) reported a soil Olsen-P threshold of 10 mg/kg, indicating that even soil P concentrations at agronomic optimum will negatively impact on the surrounding environment. This is in contrast to Sibbesen and Sharpley (1997) who suggested that critical extractable soil P concentrations that were detrimental to water quality were well above agronomic optimum. This contradiction is not surprising when we consider the large potential variation in P sorption capacity from one soil to another. Further investigation of surface runoff P concentrations across a range of P sorption capacity soils, and soil extractable P concentrations, is warranted.

Even once a relationship between P sorption capacity, soil P concentration, and P loss is thoroughly defined, an international threshold may not be appropriate. For example, an Australian Ferrosol with an Olsen-P of 60 mg/kg was reported by Burkitt *et al.*, (2010b) to have dissolved reactive P (DRP) concentrations in surface runoff which were approximately ten fold greater than those reported by McDowell and Sharpley (2001) for USA and United Kingdom (UK) soils at similar Olsen-P concentrations. Melland (2003) and Dougherty (2006) also reported greater surface P losses for a given Australian soil P concentration than reported by McDowell and Sharpley (2001) and those reviewed by Vadas *et al.*, (2005) for USA and UK soils. This suggests that, compared to younger less weathered soils, many Australian soils may have a greater tendency for P loss for a given extractable soil P concentration. Differences in geomorphology, age, bioclimate (Birkeland, 1984), and pH (Barrow, 1984; Murphy and Sims, 2012) between soils could contribute to different relationships between P sorption capacity, soil extractable P concentration, and P loss.

PASTURE PRODUCTION AS SOIL P CONCENTRATIONS DECREASE

Phosphorus utilisation has been recommended as a best management practice for soils excessively concentrated with P (Tunney *et al.*, 1997; Walker, 2005). Data from long-term trials suggest that reducing excessive soil P concentrations have no large impacts on crop yield, unless they decrease below agronomic optimum (McCollum, 1991; Johnston and Poulton, 1992; Withers *et al.*, 1994; Watson *et al.*, 2007). Thus, the decrease in pasture production reported by Dodd *et al.*, (2012) for one of their four trial sites was not surprising since their initial Olsen-P concentrations were close to their specified agronomic optimum of 25 mg/kg (7.5 cm sampling depth), and below optimum at the end of the study. In addition, no mention was made of whether other nutrients such as potassium and sulphur were above agronomic optimum.

Withers *et al.*, (2005) suggested that different critical values may be necessary when P application is withheld – as distinct from the critical values when P is being added. This is based upon desorption curves reflecting sequential extraction from progressively less labile stores and the time required for this P to be released as soil P concentrations decrease. This contrasts with sorption curves which reflect the rate of fixation as labile and soil solution P concentrations increase. However, soils with extractable P concentrations in excess of agronomic optimum should contain enough P for optimum plant production, irrespective of whether these concentrations are being built-up or drawn upon. Since larger P inputs are required to increase highly buffered soils to a given extractable soil P concentration, there may be more P available in such soils to replenish the soil solution for a longer period than low P buffering soils. Further knowledge of how long excessive extractable soil P concentrations can be utilised, according to a soils buffering capacity, is required.

REDUCING EXTRACTABLE SOIL P CONCENTRATIONS

Currently there are large areas of intensively grazed dairy pasture soils in Australia which have extractable soil P concentrations above the agronomic optimum (National Land and Water Resources Audit, 2001). Similarly, some international soils are also excessively concentrated with P (Sharpley *et al.*, 1994; Tunney *et al.*, 1997; Leinweber *et al.*, 2002). Yli-Halla *et al.*, (2002) and Koopmans *et al.*, (2004) reduced extractable soil P concentrations by omitting P fertiliser and utilising excessive soil P through cropping potted soils with grass under glasshouse conditions. Field trials supporting pot trial findings are scarce, but necessary, since the results of pot studies cannot be directly transferred to practice due to factors such as the thickness of the soil layers being restricted to the surface 5 and 10 cm for the Koopmans *et al.* (2004) study, for example.

Ideally, field studies should be undertaken over several years, and the extractable soil P concentrations should be well in excess of agronomic optimum. If these two factors are not incorporated into a field study, the results may be misleading. Short-term field studies e.g. two and a half years, have typically reported linear decreases in extractable P (Batten *et al.*, 1979; Burkitt *et al.*, 2002a). In comparison, longer-term studies have shown decreases with time to be exponential (Johnston and Poulton, 1992; Herlihy *et al.*, 2004; Schulte *et al.*, 2010; Dodd *et al.*, 2012), i.e. the decrease in extractable soil P concentration decreases with time and approaches an asymptote. Exponential decreases in soil P occurs through the sequential

exhaustion of progressively less labile P stores. Decreases in labile P stores are the most rapid, but the rate of decline subsequently decreases as less labile stores are drawn upon. If excessive soil P concentrations are not included, linear or no significant decreases may be observed (Cayley and Kearney, 1999; Dodd and Ledgard, 1999). For example, Watson *et al.*, (2007) only reported a small although significant change in the Olsen-P concentration of grassland soil after five years of no P fertiliser application when the initial Olsen-P concentration of the surface 7.5 cm was 23 mg/kg, and estimated export in liveweight gain was 8.4 kg P/ha.yr. This is due to the smaller amount of P exported when compared to excessively concentrated soils, and replenishment of P through mineralisation and solubilisation of OM and Po by micro-organisms.

The greater the extractable soil P concentration, the greater the amount of P available to be lost, exported, and sorbed, and the greater the decrease in extractable soil P as these losses occur. Plant and animal uptake of P increases with extractable soil P concentrations, until their maximum concentration is reached. The greater the quantity of plant material removed, i.e. through grazing, removal of hay and silage, and/or animal excreta transfer, and the greater their concentrations, the greater the quantity of P exported from the soil. Thus, the depletion of excessive soil P concentrations by exporting various quantities of P in fodder has been reported (Herlihy *et al.*, 2004; Schulte *et al.*, 2010). Schulte *et al.*, (2010) modelled several scenarios of varying P exports/P balances and their influence on extractable soil P concentration decreases. However, McCollum (1991) reported that even when the P exported in maize and soybean was replaced, extractable soil P still decreased. Decreases were larger in soils with greater initial extractable P concentrations, due to continued sorption.

Exponential decreases in extractable soil P are influenced by continued adsorption of P (Barber, 1979; McCollum, 1991). Barrow (1998; 2002) reported that the capacity of soil to sorb subsequent P fertiliser additions was less if high quantities of P were previously applied. Thus, subsequent P fertiliser additions are held in a more readily available form (Barrow, 1974a; Barrow *et al.*, 1998; Bolland and Allen, 2003). This more available P is subject to chemical reactions with soil constituents i.e. conversion to unextractable forms through precipitation, and absorption, as alluded to by Herlihy *et al.*, (2004) and McCollum (1991), losses to surface and groundwater, and plant and animal uptake. Initially, rapid decreases in extractable soil P may be observed for soils with low PBI since they are at greater risk of sorption saturation, and resultant environmental losses (Weaver *et al.*, 1988; McDowell and Condon, 2000). In contrast, high PBI soils may also demonstrate rapid decreases in extractable soil P due to continuing P sorption (Barrow, 1978), while buffering may prolong the period of decrease when compared to medium to low PBI soils (Dodd *et al.*, 2012). For instance, McCollum (1991) found that it took >17 years for Mehlich-1-extractable P concentrations measured from a fine sandy loam, with a likely low P buffering capacity, to decrease from 99 g P/m³ to the agronomic optimum value of 20-25 g P m⁻³. Thus, soil properties most likely to influence changes in soil extractable P include those associated with P sorption.

Some replenishment of P exported and sorbed (Barrow and Campbell, 1972) can occur through mineralisation of Po (Probert and Williams, 1985; Sinclair *et al.*, 1994), solubilisation of precipitated P

(Richardson *et al.*, 2001), desorption (Schoumans and Chardon, 2003), or labile P being extracted from deeper layers in the soil via the plant (Probert and Williams, 1985). Indeed, slow release of P accumulated between 1856 and 1901 in the Exhaustion Land Experiment at Rothamsted, UK, is still occurring, evident through P concentrations of crops grown in the soil which has not since received P (Johnston and Poulton, 1997). Table 1.1 displays a selection of studies which have reported decreases in extractable soil P concentrations. Inconsistency between studies, i.e. soil P extract used, makes comparisons between studies difficult.

Due to the various factors influencing decreases in soil P concentrations, models have been developed to estimate the time required to reduce excessively concentrated soils to agronomic optimum. Dodd *et al.*, (2012) developed an equation to estimate how long it would take water extractable-P (WEP) to decrease to a concentration of 0.02 mg P/L (0.10 mg/kg) for four soils. They reported it would take ca. 22-30 years for soils at Winchmore and Lincoln, 25-44 years for soil at Whatawhata, and 26-30 years for soil at Ballantrae to decrease to the WEP threshold. The much shorter predicted time for the soils at Winchmore, was thought to be because of its lower P retention (PR) (23-29%) compared to the Whatawhata (55–71%) and Ballantrae (30–50%) soils. Dodd *et al.*, (2012) reported correlations between a β value (which represents the decrease in P concentration over time) for Olsen-P with the initial Olsen-P ($r^2=0.41$) and initial WEP ($r^2=0.78$) concentrations. Similarly, WEP concentration decreases were significantly correlated with the initial WEP ($r^2=0.56$) concentration, PR ($r^2=0.65$), quotient of PR and Olsen-P (P_i/PR) ($r^2=0.79$), and pH ($r^2=0.59$) (Dodd *et al.*, 2012). For $CaCl_2$ -P, the only significant correlation was with initial $CaCl_2$ -P ($r^2=0.43$) concentration (Dodd *et al.*, 2012). This supports the view that in addition to the PR capacity of the soil, the initial P concentration also influences the decrease in soil P.

Decreases will most likely be different for different soil pools, i.e. initially greater for labile P than non-labile P, and reflected in different soil extractions over time. Dodd *et al.*, (2012) reported WEP to decrease faster than $CaCl_2$ -P and Olsen-P concentrations. Despite this rapid decrease, the time reported by Dodd *et al.*, (2012) for Olsen-P concentrations to decrease to agronomic optimum was shorter than the time they reported for WEP concentrations to decrease to the environmental threshold. This suggests that even when excessive soil P concentrations are reduced to agronomic optimum, some soils may still pose a risk of environmental P loss.

Table 1.1. Decreases in various extractable soil P concentrations for a variety of soils, decrease periods, on-going P fertiliser (P_{fert}) rates, initial P concentrations (P_{init}), and cropping systems.

Author	Time (years)	No. Soils	Soil type	P _{fert} (kg/ha.yr)	P _{init}	Mean absolute change in soil P concentration	Model of soil P decrease	Comments
Olsen-P (mg/kg)								
Burkitt <i>et al.</i> , (2002a)	2.5	7	various	0	15.0	From 0.7 to 6.7		Control treatments. Decrease negatively related to P _{init}
Roberts <i>et al.</i> , (1994)	6	13	na	0	13.0	6.8		50-70% clippings returned
Paris <i>et al.</i> , (2004)	15	2	Ustochrept	Control	19.3	12.5	lnOlsen-P=2.9952-0.0698t, <i>r</i> =0.96 lnOlsen-P=3.2659-0.0842t, <i>r</i> =0.99	Namely wheat, maize and lucerne
Johnston and Poulton, (1977)	71	1	na	26.2	23.8	16.8	Exponential equation y=ae ^{bx}	Continuous barley
				62.4	23.2	15.9		
					60.1	49.6		
Barber (1979)	8	1	Acid Argiudoll silt loam	0	18.0	10.0	Exponential decrease	Continuously cropped corn, soybean, wheat and hay (10 yrs then corn). 15 cm cores
Halvorson and Black (1985)	17	1	Argiboroll	0	6.0	1.0		11 crops but low yields
Dodd <i>et al.</i> , (2012)	7, 16, 21, & 26	4	Alfisol, Inceptisols, & Ultisol	0	40, 45, 28, 50	10, 20, 5, 20	Exponential equation y = α x e ^{-βt}	Grassland field soils
Morgan-P (mg/L)								
Herlihly <i>et al.</i> , (2004)	4.0	31	8 soil series	0	4.3	2.6		4 years of cut and carry with no fertiliser application. Offtake of between 25 and 35 kg P/ha.yr
					12.6	8.2		
					10.0	6.2		
					20.0	12.7		
Mechlin-P (g Pm ⁻³)								
Kamprath (1999)	41.0	3	na	0, 10, 20 and 40	10.0	1.6	Regression equations for the 3 soils relating change in Mechlin-1-P (M1P) as a function of time of cropping, when zero P _{fert} applied. M1P = 97.2 - 2.81t M1P = 54.2 - 198t M1P = 10.5 - 0.53t	Mean removal in harvested grain was 17, 13.5 & 13 kg P/ha.yr. Corn & soybean grown in alternate years. Decreases reported to be linear, however, the data suggests an exponential decrease.
					54.0	6.0		
					97.0	8.4		
McCollum (1991)	26.0	1	Umbraquult	0	25.0	na	Exponential equation loge Ps = A + Bt	Corn, soybean exporting 16 kg P/ha/yr
				0	56.0	na		
				0	99.0	na		
Cope (1981)	50.0	4	na	0	13.0	6.0		Cropped cotton, vetch, corn, and wheat
	50.0	2		0	32.0	24.0		
	20.0	2		A	60.0	40.0		
	20.0	2		A	25.0	20.0		
	20.0	2		B	80.0	15.0		
	20.0	4		B	50.0	20.0		
	20.0	2		C	130.0	40.0		
	20.0	2		C	90.0	30.0		
	20.0	1		C	60.0	15.0		

A = 14 kg/ha.yr for 16 years, then 18 kg/ha.yr for 12 years, then 0 kg/ha.yr for 20 years; B = 27 kg/ha.yr for 16 years, then 36 kg/ha.yr for 12 years, then 30 kg/ha.yr for 20 years; C = 54 kg/ha.yr for 28 years, then 30 kg/ha.yr for 20 years. na = not advised.

CONCLUSION

Sustainable land management requires an understanding of soil chemical, biological, and physical processes that affect the availability of P in soil for plant uptake as well as environmental loss. Currently, knowledge is limited surrounding the rates and processes relating to decreases in agronomic and environmental soil P concentrations when P fertiliser is withheld from a range of soils and initial soil P concentrations. Needed, is development of our understanding of relationships between potential environmental P losses and a range of extractable soil P concentrations, soils and P extractions. This knowledge is essential as excessive extractable soil P concentrations are now common under intensive pasture systems. Soil P concentrations above agronomic optimum are costly – both financially and environmentally. Creation and maintenance of excessively concentrated soils through P fertiliser application put added pressure on the finite supply of raw P reserves. Until a soil P measure which relates a soil's capacity to supply P and the amount of P available has been accepted by the scientific community, and thresholds developed, depletion of extractable soil P concentrations to agronomic optimum should be encouraged. Utilising and depleting excessive soil P concentrations to agronomic optimum is an efficient means of reducing the pressure on raw P reserves while also reducing environmental impact.

2

DECREASE IN ENVIRONMENTAL AND AGRONOMIC P CONCENTRATIONS WHEN P FERTILISER APPLICATION IS REDUCED OR OMITTED FROM PASTURE SOILS WITH VARYING P STATUS

ABSTRACT

There are many intensively managed soils which contain phosphorus (P) concentrations which surpass that required for optimum production. Soils with P concentrations in excess of agronomic optimum can result in unnecessary losses of P that can adversely impact water bodies. Reducing excessive soil P concentrations is important for the economic and environmental sustainability of intensive agriculture, such as the Australian dairy industry. Despite this, there is little knowledge of decreases in extractable soil P concentrations when P fertiliser applications are reduced or omitted from soils with P concentrations and properties representative of intensive pasture grazing systems. Decreases in calcium chloride (CaCl_2 -), Olsen- and Colwell-extractable P were monitored for up to four and a half years for six Australian pasture soils with contrasting textures and P buffering indices (PBI). Sixteen thrice replicated treatments consisting of four initial extractable P concentrations (P_{init}) paired with four on-going P fertiliser rates (P_{fert}) were established for each of the six soils. An exception was an extremely low PBI soil where a range in P_{init} concentrations could not be established. The resultant decreases were larger the greater the P_{init} concentration, and the lower the rate of on-going P_{fert} . An exception was an extremely low PBI soil where decreases in initially high CaCl_2 -P concentrations were large irrespective of on-going P_{fert} . There was a greater proportional decrease in the environmentally extractable P compared to the agronomic extractable P, with mean decreases in CaCl_2 -P of -57%, Olsen-P of -25%, and Colwell-P of -12%. This study advances scientific knowledge of, and aids land and catchment managers in estimating likely changes in, extractable soil P concentrations when P fertiliser inputs are withheld or reduced.

INTRODUCTION

Phosphorus contained in runoff from agriculture can contribute to eutrophication of surface waters (Carpenter *et al.*, 1998). In Australia, surface P runoff from intensively managed dairy pastures has been widely reported, with total-P concentrations in the range of 0.9–35.0 mg/L (Nash *et al.*, 2000; Dougherty *et al.*, 2008). Since runoff P concentrations generally increase as soil extractable P concentrations increase (Sharpley and Rekolainen, 1997; Burkitt *et al.*, 2010b), it is important to ensure dairy pasture soils are not in excess of agronomic optimum; considered in Australia to be an Olsen-P within the range of 14-17 mg/kg (10 cm) (Gourley *et al.*, 2007).

Agronomically excessive soil P concentrations are common in Australian pasture soils as a result of P imports in fertilisers and livestock feeds exceeding removal in farm produce, runoff, and leaching. A national study by Gourley *et al.*, (2010) found that 80% of 1773 pasture paddocks from 37 conventional dairy farms sampled across Australia had Olsen-P concentrations above agronomic optimum (mean 36 mg/kg), with 50% of these paddocks one and a half times, and 20% at least three times agronomic optimum.

Where extractable soil P concentrations are already excessive, omitting or applying less P fertiliser than is exported in produce may result in a decrease in soil P. This is likely to be an economically attractive solution since there are no implementation costs, and there is likely to be no production penalty whilst extractable soil P concentrations remain near or above the agronomic optimum. However, there has been little research on reducing or omitting P fertiliser application from soils that reflect the range of extractable soil P concentrations found on Australasian dairy farms, and intensive pastures internationally, where soil P concentrations were reached through mineral P fertiliser application. Existing studies of decreases in extractable soil P concentrations are difficult to compare due to the range of soil P extractions and sampling depths employed. While some knowledge has been gained from trial sites which were established to assess pasture response to fertiliser, soils with high extractable P concentrations are not usually included as they are non-responsive (Roberts *et al.*, 1994). In addition, studies can be relatively short e.g. two and a half years (Batten *et al.*, 1979; Burkitt *et al.*, 2002a) when compared to the potential time frame required to identify extractable soil P decrease trends. Thus, linear decreases have typically been reported for short-term studies, while long-term studies have shown decreases to be exponential. However, long-term trials are usually limited to one soil (Cope, 1981; McCollum, 1991; Poulton, 1995), with no studies successfully relating soil characteristics to extractable soil P decrease (Kamprath, 1999; Paris *et al.*, 2004; Dodd *et al.*, 2012). For some studies where more than one soil was included, there were only two replicates (Herlihy *et al.*, 2004), or none (van der Salm *et al.*, 2009).

In order for a range of extractable soil P concentrations to be established, P inputs are required. This can occur through historical mineral and manure P inputs over a relatively long period of time or through application of mineral P fertiliser over a short period e.g. over 12 months. Over 26 years, McCollum (1991) reported greater absolute decreases for a fine sandy loam soil with high initial extractable soil P

concentrations relative to low initial concentrations, with no differences in rates or patterns of decrease irrespective of whether the concentrations were built-up through a single application (of up to 648 kg P/ha) or over an eight year period. Upon application to soil, fertiliser P commences a process of physical and chemical redistribution, with a subsequent decrease in the soluble P pool with time. The majority of these processes occur within the first few hours of contact between fertiliser and soil (Agbenin and Tiessen, 1995), meaning that six months after P fertiliser application, similar processes which influence extractable soil P should be expected to occur as for soil which had received P fertiliser several years earlier. Indeed, it is the slow P sorption reaction which could be considered more important than the initial rapid reaction in controlling soil P availability and any residual effect of added fertiliser P. Slow P reactions have been reported to be independent of the amount of P fertiliser applied (Barrow and Shaw, 1975), with Barrow (1987) citing that many studies have shown that the proportion of the P applied which is converted to non-labile P is independent of the P fertiliser rate. In addition, while manure applications are often considered to mainly consist of Po, the majority is in fact inorganic P (Pi) (Guppy and McLaughlin, 2009), which may be subject to similar conversions and immobilisation as Pi applied via mineral fertilisers. This is supported by the ratio of Pi to Po being reported to be similar for soils irrespective of whether fertilised with similar amounts of mineral or manure P (Guggenberger *et al.*, 2000).

Extractable P decreases are likely to be affected by a number of system nutrient balances and soil properties. Phosphorus decreases have been reported to be larger the higher the extractable soil P concentration (McCollum, 1991; Kamprath, 1999; Herlihy *et al.*, 2004; Dodd *et al.*, 2012). This is thought to be due to previous applications of P reducing the P sorption capacity (PSC) and P buffering index (PBI) of soils due to a greater degree of sorption saturation, resulting in more P being held in an available form (Barrow, 1974a; Barrow *et al.*, 1998; Bolland and Allen, 2003). Phosphorus buffering index is used in Australia as an index of a soil's PSC. Soils with coarse textures, low clay, oxalate-extractable aluminium (OxAl), and oxalate-extractable iron (OxFe) contents, and low resultant PBIs and PSCs, have been reported to have lower abilities to retain applied P (Russell, 1960; Ozanne *et al.*, 1961; Lewis *et al.*, 1981), than fine textured soils with higher clay, OxAl, and OxFe contents, and greater PBIs and PSCs. Indeed, soils with initially low PBI are at greater risk of sorption saturation, environmental losses (Weaver *et al.*, 1988; McDowell and Condron, 2000), and potentially rapid decreases in extractable P concentrations. However, high PBI soils, with greater PSCs, may also demonstrate rapid decreases in extractable P due to continuing sorption (Barrow, 1978), while buffering may prolong the period of decrease when compared to medium to low PBI soils (Dodd *et al.*, 2012). Thus, soil properties most likely to influence extractable soil P changes include those associated with P sorption.

Oxalate-Al and OxFe are usually associated with the surface of clay and organic matter (OM) (Sample *et al.*, 1980), and increase a soils capacity to sorb P (Condron and Goh, 1989; McDowell and Condron, 2001; Burkitt *et al.*, 2002b). Organic matter can alter the crystallinity and surface area of OxAl and OxFe, which has been reported to indirectly decrease (McDowell and Condron, 2001), and increase (McLaughlin *et al.*, 1981), P sorption. McDowell and Condron (2001) concluded that the chemical composition – rather than the quantity – of OM affects its role in P sorption. Removal of OM has been reported to increase or decrease P sorption,

depending on the equilibrium pH values and soil types (Hiradate and Uchida, 2004). Although sorption in soils with low pH are typically considered to be controlled by OxAl and OxFe (Sample *et al.*, 1980; McDowell *et al.*, 2003), soil pH has been reported to have a variable effect on P sorption, according to soil (Murphy, 2007; Murphy and Stevens, 2010).

In order to assess the effect of reducing or omitting P fertiliser from pasture soils on environmental (CaCl_2 -) and agronomic (Olsen- and Colwell-) soil P, a range of soils with contrasting PBIs, initial P (P_{init}) concentrations, and on-going P fertiliser rates (P_{fert}) were monitored for up to four and a half years.

MATERIALS AND METHODS

Trial site management and soil characterisation

Six field trial sites were established in May 2005 on non-irrigated commercial grazing properties across northern Tasmania. Annual rainfall during trial monitoring ranged from 627–1243 mm, according to site, which was slightly lower than the long-term mean annual rainfall of 899–1450 mm across the sites (Bureau of Meteorology, 2012a). All soils supported pasture established at least five years before trial establishment, comprising predominantly of perennial ryegrass (*Lolium perenne* L.), and did not need to be re-seeded. All soils were grazed rotationally at varying stocking rates by dairy or beef cattle. Phosphorus exports in animal products were not directly measured for each plot. Instead P exports were approximated by combining estimated pasture P concentrations and removal based on work by Cotching and Burkitt (2011), and Burkitt *et al.* (2010a), and whole farm nutrient budgets. Between 2.9 and 12.3 kg P/ha.yr was estimated to be exported according to trial site and P_{init} concentration. Due to the short grazing periods i.e. <13 hours, 12 months of manure deposit monitoring suggested that no area of the trial sites were receiving more manure than others.

Sites were selected to represent the broad range of soils used for pasture production in south eastern Australia (Burkitt *et al.*, 2001; Burkitt *et al.*, 2006), encompassing a variety of P sorption capacities and textures (sand to clay loam). Soils were also selected for their moderate extractable P concentrations (five of the six soils had Olsen-P concentrations ≤ 18 mg/kg, the sixth being 37 mg/kg). Soil samples for basic characterisation (Table 2.1) were collected prior to trial commencement by taking fifty soil cores (2.5 cm diameter by 10 cm depth) randomly across each 0.1 ha site.

All soil samples were oven dried at 40°C for 72 h and ground to pass a 0.2 cm sieve. Samples were analysed for Olsen- (Olsen *et al.*, 1954) and Colwell- (Colwell, 1963) extractable P, pH (H_2O and CaCl_2) (1:5 soil:solution ratio and 0.01 M CaCl_2) (Rayment and Lyons, 2011), cation exchange capacity (Gillman and Sumpter, 1986), organic carbon (C) content (Walkley and Black, 1934), perchloric acid total-P (Sommers and Nelson, 1972), P_o [difference between total and P_i using 0.5 MH_2SO_4 ; (Blakemore *et al.*, 1987)], oxalate-extractable aluminium (OxAl) and iron (OxFe) (Schwertmann, 1964), P sorption capacity (PSC), and unadjusted PBI (Burkitt *et al.*, 2008). Phosphorus sorption capacity was calculated as estimated by Borling *et al.*, (2001) using 0.5 as the alpha scaling factor i.e. $\text{PSC} = 0.5(\text{OxAl} + \text{OxFe})$. Briefly, PBI was measured by shaking 1 g of soil

for 17 h in 0.01 M CaCl₂ with an addition of 1000 mg P/kg soil. The difference between the added P and the final P concentration in the equilibrating solution was the amount of P sorbed, with PBI calculated as P sorbed (mg/kg) / [final P solution (mg/L)^{0.41}] (Burkitt *et al.*, 2008). Soil particle size was determined using the pipette method (Piper, 1947), and soil texture assigned based on the soil texture triangle of Marshall (1947) for International Soil Texture Classification (Atterberg, 1905).

Treatments

For each soil, sixteen treatments (four P_{init} concentrations by four on-going P_{fert} rates) were contained in 2 by 10 m plots arranged in a randomised thrice replicated block design. Triple superphosphate (20% P, 14% Ca and 1% S) was surface applied by hand during site establishment to create the four P_{init} concentrations (Table 2.2), except the lowest P_{init} concentration which did not receive establishment fertiliser. Each plot also received surface application of yearly P_{fert} rates of either 0, 0.5, 1 or 2 times estimated maintenance P (Table 2.2) which were split and applied every six months (late autumn and late spring), commencing at establishment. Yearly P_{fert} ranged from 0 to 50 kg P/ha (Table 2.2), increasing as PBI increased, and was based on work by Gourley *et al.*, (2001) and Cayley and Kearney (1999).

Re-application of the same rate of establishment fertiliser twelve months after the initial application, total ranging from 172 to 1644 kg P/ha, according to soil (Table 2.2), was required to obtain the two highest P_{init} concentrations. Thus, the two highest P_{init} concentrations were monitored over the subsequent three years, the second lowest concentrations over four years, the lowest concentrations receiving P_{fert} over four years, and the control over four and a half years.

Soil sampling and analyses

Every sixth month, from May 2005 to November 2009, immediately before each P_{fert} application, fifteen soil cores (0-10 cm) were taken from each plot, bulked, oven dried at 40°C for 72 h, and ground to pass through a 0.2 cm sieve. All samples were analysed for Olsen-P and Colwell-P.

Every twelfth month, starting in November 2005, 0.01 M CaCl₂-P (Houba *et al.*, 2000) was measured for P_{ferts} 0, 1 and 2 of the two lowest P_{init} concentrations. From November 2006, the same P_{fert} treatments for the highest P_{init} concentration were also measured. The CaCl₂-P extractions commenced four and a half years after trial establishment using stored soil samples in which Olsen-P and Colwell-P had been determined earlier. The treatments selected for CaCl₂-P analysis were based on trends observed for Olsen-P and Colwell-P. Calcium chloride extraction of surface soil has been related to dissolved reactive P measured in surface runoff (McDowell *et al.*, 2001b). The low ionic strength of the extracting solution simulates the dissolution and desorption of P from soil particles (Bloesch and Rayment, 2006) that are readily available for plant uptake or movement in soil water and runoff, and this extract is often used as an environmental measure of P runoff risk.

Statistical analyses

Before and after establishment fertiliser application, some replicate plots were consistently higher or lower than others. In addition, some plots did not align with the target P_{init} concentrations (Figures 2.1-2.3). As a result, each variable was naturally log-transformed, with the means and standard errors (s.e.) presented on the log scale in Table 2.3. Analysis of variance (ANOVA) was used to assess the influence of establishment fertiliser and P_{fert} on P_{init} concentration, and changes in $CaCl_2$ -P, Olsen-P and Colwell-P concentrations. A repeated measures approach was taken, with an autoregressive correlation structure for P_{init} , and P_{fert} , and their interaction, and a random effect per soil. Time was measured in six month intervals for Olsen-P and Colwell-P, and twelve month intervals for $CaCl_2$ -P. Soil characteristics measured before trial establishment were regressed against mean change in $CaCl_2$ -P, Olsen-P and Colwell-P for each variable and soil. Absolute differences in unlogged concentrations of each of the three P extracts between the P_{init} and final P concentrations were calculated, and assessed using a *t*-test. All statistical analyses were generated using SAS software 9.2 (SAS Institute Inc, 2008).

Table 2.1. Selected chemical and physical properties of the surface 10 cm of pasture soils sampled from six field sites located in north-west Tasmania, prior to P fertiliser treatment

Characteristic	Soil					
	1	2	3	4	5	6
Soil Texture ^B	Silty Loam	Loam	Sand	Sandy Loam	Silty Clay Loam	Sandy Loam
Clay (%) <0.002 mm	23	20	6	11	18	14
Sand (%) 0.02 – 2 mm	47	58	90	70	51	77
Silt (%) 0.002 – 0.02 mm	30	22	4	19	31	9
pH ($CaCl_2$)	5.4	4.8	3.9	4.9	4.8	4.6
Olsen-P (mg/kg)	12	12	16	18	18	37
Colwell-P (mg/kg)	40	39	30	43	69	72
Organic C (g/kg)	95	28	114	26	60	87
CEC (cmol _c /kg)	21	9	19	5	24	13
Oxalate-extr. Al (mg/kg)	5900	2600	300	700	5200	800
Oxalate-extr. Fe (mg/kg)	4700	4000	800	2300	12300	700
PBI ^A	480	220	<10	60	400	60
PSC ^D (mmol/kg)	151	84	13	34	206	21
Soil Classification ^C	Red Ferrosol	Brown Kurosol	Podosol	Grey Dermosol	Brown Dermosol	Hydrosol

^A Phosphorus buffering index unadjusted (Burkitt *et al.*, 2008); ^B International Soil Texture Classification System (Atterberg, 1905);

^C Australian Soil Classification (Isbell, 2002); ^D Phosphorus Sorption Capacity (Borling *et al.*, 2001).

Table 2.2. Establishment fertiliser applied to create P_{init} concentrations across all P_{fert} rates P_{fert} rates were split into twice yearly applications, directly after soil sampling

Treatment	Soil					
	1	2	3	4	5	6
P_{init} category	Establishment fertiliser (kg P/ha)					
1.0	0	0	0	0	0	0
2.0	189	83	20	77	96	89
3.0 [†]	708	386	172	294	392	304
4.0 [†]	1644	930	500	644	792	860
P_{fert} rate	P_{fert} rate (kg P/ha.yr)					
0.0	0	0	0	0	0	0
0.5	13	10	5	10	13	7
1.0	25	20	10	20	25	15
2.0	50	40	20	40	50	30

[†]Total amount of P applied after the initial application was repeated 12 months later in order to reach target P_{init} concentrations.

RESULTS AND DISCUSSION

Soil characterisation

The soils ranged in texture and P sorption, with PBI values ranging from 6–519, and OxAl and OxFe contents ranging from 300 to 5900, and 700 to 12300 mg/kg, respectively (Table 2.1). Phosphorus sorption capacity, calculated using an alpha value of 0.5, ranged from 13 (Soil 3) to 205 (Soil 5). Most of the soils were moderately acidic (pH CaCl_2 4.6–5.4) with Soil 3 very acidic (pH CaCl_2 3.9). Organic-C ranged from 26 g/kg at Soil 4 to 114 g/kg for the extremely low PBI Podisol (Soil 3). It was this variety in characteristics between soils which influenced P_{init} concentrations, and decreases in soil P concentrations over time.

Influence of P fertiliser on initial CaCl_2 -P, Olsen-P and Colwell-P concentrations

Application of P fertiliser at site establishment significantly ($P < 0.001$) changed initial CaCl_2 -P, Olsen-P and Colwell-P concentrations when all soils were analysed together. Distinct P_{init} concentrations were created for all soils except Soil 3 (Figures 2.1-2.3). Olsen-P and Colwell-P concentrations of Soil 3 ranged from 5-26 and 8-44 mg/kg, respectively, even after the second establishment fertiliser was applied. Olsen-P and Colwell-P concentrations of the other soils ranged from 12-111 and 30-433 mg/kg, respectively (Figures 2.1-2.3). In contrast, CaCl_2 -P concentrations of Soil 3 were high, ranging from 2.9 to 47.6 mg/kg, when compared to those reported by other researchers (McDowell and Sharpley, 2001; Dougherty *et al.*, 2008; Burkitt *et al.*, 2010b). However, these extreme CaCl_2 -P concentrations were not large enough to account for all of the applied P. Phosphorus applied to Soil 3 may have been lost from the surface 10 cm sampling depth due to the soil's extremely low PBI, coarse texture (Table 2.1), and the ~1100 mm annual rainfall. In addition, some of the P applied to Soil 3 may have been converted to forms not extractable by CaCl_2 or bicarbonate through

precipitation, incorporation into the soil OM via plant uptake, and/or immobilised as Po through microbial uptake. The microbial population of Soil 3 may also have been larger than the other soils since it contained the greatest organic-C content, and microbial-C has been reported to represent a greater proportion of organic-C in sandy than clay and silt loam textured soils (Sparling, 1992). Thus, greater immobilisation of Pi to Po may have occurred for Soil 3 than the other soils.

Initial Olsen-P and Cowell-P concentrations were not significantly ($P>0.05$) altered by the single application of P_{fert} during P_{init} establishment (Table 2.3). This may in part be due to the single application of P_{fert} being small compared to the establishment P fertiliser. However, even the maximum P_{fert} application of 10-25 kg P/ha, varying according to soil (Table 2.2), did not significantly ($P<0.05$) increase the P_{init} concentrations of Category 1, which did not receive establishment fertiliser (Table 2.3). Since Burkitt *et al.*, (2001) reported 5-16 kg P/ha.yr above maintenance was required to increase Olsen-P by 1 mg/kg, depending on PBI, no significant ($P>0.05$) increase in P_{init} due to P_{fert} was expected. However, $CaCl_2$ -P concentration of Category 1, which received 0 P_{fert} (control), was significantly ($P<0.05$) lower than the same category which had received P_{ferts} 1 or 2. This indicates the sensitivity of the $CaCl_2$ extraction to the changes in soil P concentrations after the single P_{fert} application, when no establishment P fertiliser was applied.

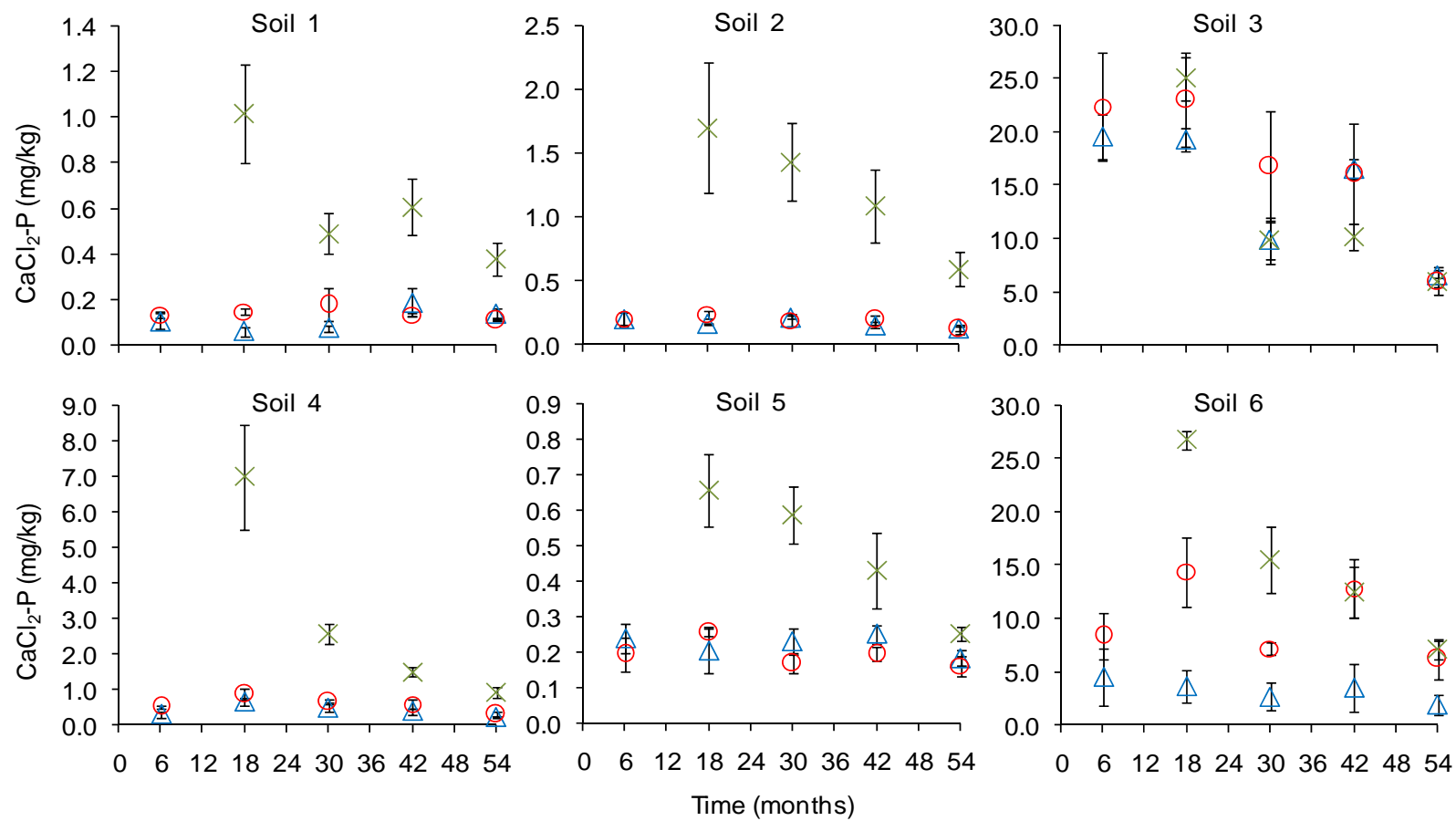


Figure 2.1. Mean $\text{CaCl}_2\text{-P}$ of the three targeted P_{init} concentration ranges; 1 (Δ), 2 (\circ), and 4 (\times), when no maintenance P_{fert} was applied. Note y-axes vary between soils.

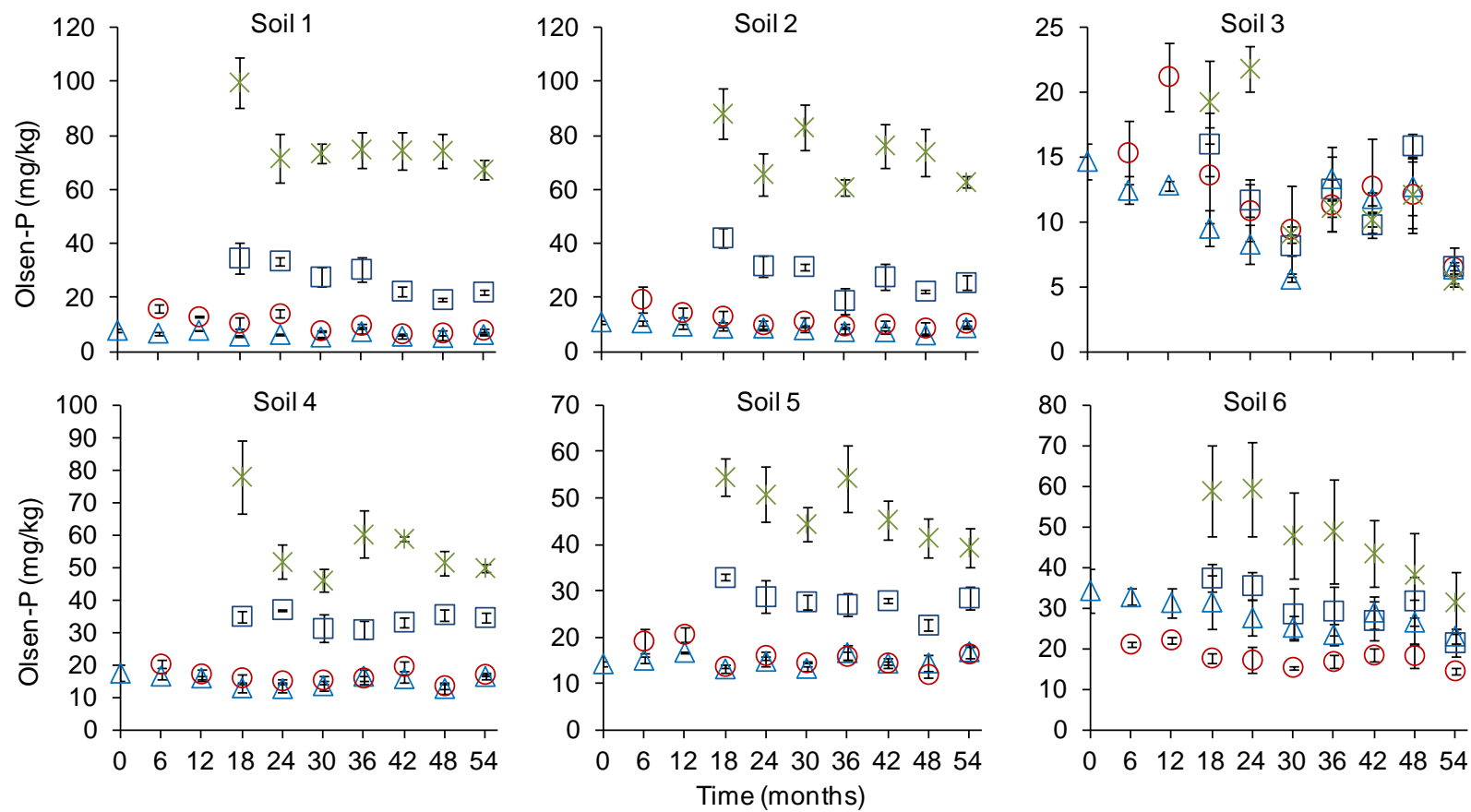


Figure 2.2. Mean Olsen-P concentration for each of the four targeted P_{init} concentrations; 1 (Δ), 2 (\circ), 3 (\square) and 4 (\times), when no maintenance P_{fert} was applied. Note y-axes vary between soils.

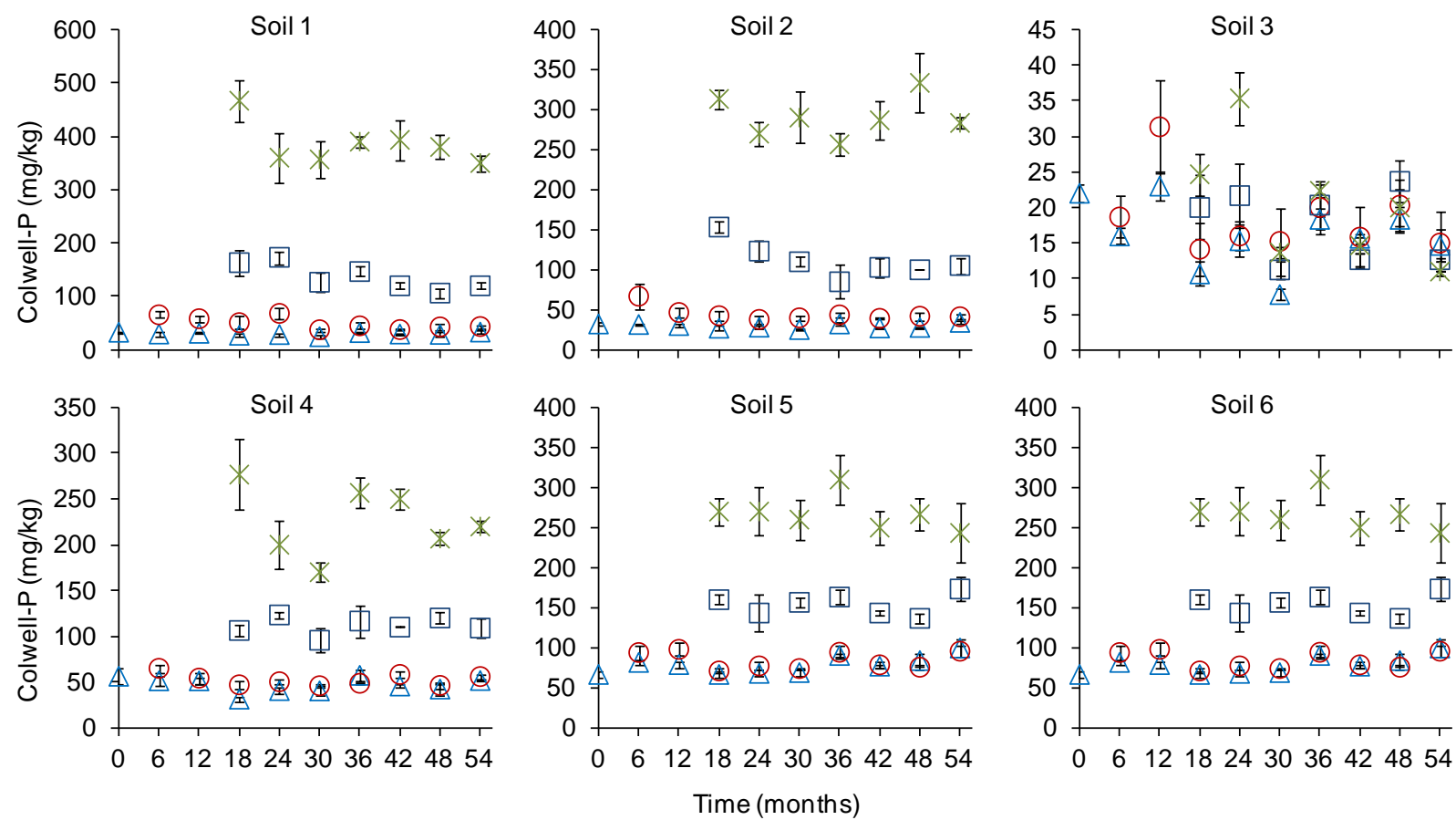


Figure 2.3. Mean Colwell-P concentration for each of the four targeted P concentrations; 1 (Δ), 2 (\circ), 3 (\square) and 4 (\times), when no maintenance P_{fert} was applied. Note y-axes vary between soils.

Change in extractable P concentrations over time according to P_{init} concentration, P_{fert} and soil

Analysis of variance across all soils showed a significant ($P < 0.001$) interaction between P_{init} , P_{fert} , and time, on the change in all three extracts. The P_{fert} effect of the current study is consistent with the findings from other studies which also identified soil (Burkitt *et al.*, 2002a) and P_{init} (McCollum, 1991; Burkitt *et al.*, 2002a; Herlihy *et al.*, 2004) as factors influencing extractable P decrease.

While the monitoring period of this study was not long enough to present decline trends for individual P_{init} treatments, the varying decreases according to P_{init} concentration indicated to the overall trend. Larger decreases generally occurred with smaller P_{fert} rates and with greater P_{init} concentrations (Table 2.3) (McCollum, 1991; Kamprath, 1999; Herlihy *et al.*, 2004). Barrow (1998; 2002) reported that the capacity of soil to sorb subsequent P fertiliser additions was less if high amounts of P were previously applied because this led to fewer available P sorption sites (greater degree of sorption saturation and a decrease in PBI), with lower P sorption energies (Ryden *et al.*, 1977). Thus, subsequent P fertiliser additions were held in a more readily available form which was subject to chemical reactions with soil constituents i.e. conversion to unextractable forms through precipitation, and absorption, as alluded to by Herlihy *et al.*, (2004) and McCollum (1991), losses to surface and groundwater, and/or incorporation into Po through uptake by plants and micro-organisms.

It could be argued that greater decreases may have occurred in the current study for the higher P_{init} concentrations than would be expected if the same amount of P fertiliser was applied over a longer period. Equally, it could be argued that different decreases may be observed if P_{init} concentrations were achieved through manure application instead of fertiliser inorganic P. However, similar decrease trends and rates have been reported for soils with high P_{init} concentrations established over both short (through a single large application of P) and long periods (over eight years) (McCollum, 1991). The results of McCollum (1991) show that the processes which influence decreases in extractable soil P are likely to occur irrespective of P fertiliser rate. Indeed, slow P reactions have been reported to be independent of the amount of P fertiliser applied (Barrow and Shaw, 1975). Similarly, Barrow (1987) reported that many studies have shown that the proportion of the P applied which is converted to non-labile P is independent of the P fertiliser rate. It was based upon the assumption that results would be broadly similar, that Barrow *et al.*, (1998) compared sorption capacity and efficiency of P fertiliser applied to eight soils which had previously received between 200 and 900 kg P/ha, according to soil, in a single application. Similar decreases in soil P built-up via manure application as those observed in this study may also be expected since a large percentage of P in manure is in fact inorganic (Guppy and McLaughlin, 2009). In addition, historical grazing animal manure deposition, and fertiliser P, would have contributed to the soil P concentrations of these soils before treatment fertiliser application.

Initial P Category 1 showed some of the smallest decreases in extractable soil P concentrations (Table 2.3; Figures 2.1-2.3). Low Olsen-P concentrations (< 10 mg/kg) have been reported not to change, even when low fertiliser rates (10 to 30 kg P/ha.yr) cease (Dodd and Ledgard, 1999; Herlihy *et al.*, 2004). Burkitt *et al.*, (2002a) reported greater decreases in extractable P concentration when Olsen-P and Colwell-P concentrations

were >15 mg/kg and >60 mg/kg, respectively. Low decreases at low extractable P concentrations are attributed to Po mineralisation through microbial activity (Sinclair *et al.*, 1994) and P desorption as soil solution P decreases (Schoumans and Chardon, 2003). Thus, low P concentrations can be expected to remain relatively stable for a long period.

When on-going P_{ferts} 1 and 2 were applied, the initially low Olsen-P and Colwell-P concentrations remained constant (i.e. Olsen-P Category 1 receiving P_{fert} 1) or increased (i.e. Olsen-P Category 1 receiving P_{fert} 2, and Colwell-P receiving P_{ferts} 1 or 2) (Table 2.3). However, there was a lack of increase in CaCl_2 -P concentrations for P_{init} Category 1, despite the greatest on-going P_{fert} rates ranging from 10-25 kg P/ha, according to soil (Table 2.2). This may have been due to the extremely high initial CaCl_2 -P concentrations of Soils 3 and 6, and their resultant large decreases over time. The large decreases in CaCl_2 -P for the lowest PBI soil's suggests P may have moved from the surface sampled 10 cm through surface runoff or leaching. In contrast, continuing slow reactions between soil and P (Barrow and Campbell, 1972) would most likely have contributed to decreases in extractable P concentrations for the majority of the other soils with greater PBIs. Indeed, the decrease in Colwell-P concentrations were not as large as CaCl_2 -P and Olsen-P concentrations (Table 2.3), indicative of the larger percentage of sorbed P recovered by the Colwell extraction. Possible reasons for the decrease in extractable soil P concentrations include P exports in milk, surface runoff, leaching, and conversion of P into pools not CaCl_2 or bicarbonate extractable i.e. Po, absorbed P, and precipitated P.

Table 2.3. Log transformed P_{init} concentrations and slope of change according to P_{init} concentration, P_{fert} rate, and soil

Within a column heading, differences between letters indicate significant differences between variables at the $P=0.05$ level. Values within brackets are standard errors

Variable	Initial CaCl ₂ -P	CaCl ₂ -P slope	Initial Olsen-P	Olsen-P slope	Initial Colwell-P	Colwell-P slope
<i>$P_{init} : P_{fert}$</i>						
<i>Across all soils</i>						
1 : 0	-0.3 (0.3)a	-0.04 (0.03)c	2.6 (0.12)a	-0.02 (0.02)c	3.6 (0.14)a	0.00 (0.02)bc
2 : 0	0.1 (0.3)b	-0.06 (0.03)c	2.9 (0.12)b	-0.06 (0.02)ab	3.9 (0.14)b	-0.03 (0.02)ab
3 : 0	na	na	3.5 (0.17)c	-0.06 (0.02)ab	4.6 (0.18)c	-0.04 (0.02)a
4 : 0	2.0 (0.3)c	-0.20 (0.05)a	4.2 (0.17)d	-0.07 (0.02)a	5.3 (0.18)d	-0.05 (0.02)a
1 : 0.5	na	na	2.6 (0.12)a	-0.02 (0.02)c	3.5 (0.14)a	0.00 (0.02)bc
2 : 0.5	na	na	2.9 (0.12)b	-0.03 (0.02)bc	4.0 (0.14)b	-0.02 (0.02)b
3 : 0.5	na	na	3.6 (0.17)c	-0.05 (0.02)ab	4.6 (0.18)c	-0.03 (0.02)ab
4 : 0.5	na	na	4.2 (0.17)d	-0.06 (0.02)ab	5.3 (0.18)d	-0.04 (0.02)a
1 : 1	0.2 (0.3)b	-0.06 (0.03)c	2.6 (0.12)a	0.00 (0.02)d	3.6 (0.14)a	0.02 (0.02)c
2 : 1	0.1 (0.3)b	-0.07 (0.03)c	3.0 (0.12)b	-0.02 (0.02)c	4.1 (0.14)b	0.01 (0.02)c
3 : 1	na	na	3.5 (0.17)c	-0.03 (0.02)bc	4.6 (0.18)c	0.00 (0.02)bc
4 : 1	2.0 (0.3)c	-0.20 (0.04)a	4.2 (0.17)d	-0.07 (0.02)a	5.4 (0.18)d	-0.05 (0.02)a
1 : 2	0.2 (0.3)b	-0.05 (0.03)c	2.7 (0.12)a	0.01 (0.02)d	3.7 (0.14)a	0.03 (0.02)c
2 : 2	0.3 (0.3)b	-0.06 (0.03)c	3.0 (0.12)b	0.00 (0.02)d	4.0 (0.14)b	0.02 (0.02)c
3 : 2	na	na	3.6 (0.17)c	-0.03 (0.02)bc	4.6 (0.18)c	-0.01 (0.02)b
4 : 2	1.8 (0.3)c	-0.15 (0.04)b	4.1 (0.17)d	-0.04 (0.02)bc	5.3 (0.18)d	-0.03 (0.02)ab
<i>$P_{init} : P_{fert}$</i>						
<i>Across all soils and P_{fert} rates</i>						
1 : all	0.03 (0.3)a	-0.05 (0.04)a	2.6 (0.12)a	-0.01 (0.02)d	3.6 (0.14)a	0.01 (0.02)d
2 : all	0.2 (0.3)a	-0.06 (0.03)a	3.0 (0.12)b	-0.03 (0.02)c	4.0 (0.14)b	-0.01 (0.02)c
3 : all	na	na	3.6 (0.17)c	-0.04 (0.02)b	4.6 (0.18)c	-0.02 (0.02)b
4 : all	1.9 (0.3)b	-0.18 (0.05)b	4.2 (0.17)d	-0.06 (0.02)a	5.3 (0.18)d	-0.04 (0.02)a
<i>Soil</i>						
<i>Across all P_{init} concentrations and P_{fert} rates</i>						
1	-1.4 (0.3)a	-0.04 (0.03)e	3.3 (0.15)b	-0.03 (0.02)c	4.7 (0.16)c	-0.01 (0.02)c
2	-0.6 (0.3)b	-0.09 (0.04)cd	3.4 (0.14)c	-0.04 (0.02)bc	4.5 (0.16)b	-0.01 (0.02)c
3	3.4 (0.3)e	-0.15 (0.04)a	3.0 (0.14)a	-0.09 (0.02)a	3.2 (0.16)a	-0.05 (0.02)b
4	0.8 (0.3)c	-0.14 (0.04)ab	3.4 (0.14)c	-0.02 (0.02)c	4.5 (0.16)b	-0.02 (0.02)c
5	-0.8 (0.3)b	-0.06 (0.03)de	3.3 (0.14)bc	-0.02 (0.02)c	4.8 (0.16)d	-0.03 (0.02)cb
6	2.8 (0.3)d	-0.11 (0.03)bc	3.7 (0.14)d	-0.05 (0.02)b	4.5 (0.16)b	-0.07 (0.02)a
<i>Across all P_{init} concentrations, P_{fert} rates, and soils</i>						
All	0.7 (0.3)	-0.10 (0.04)	3.3 (0.14)	-0.04 (0.02)	4.4 (0.16)	-0.03 (0.02)

After reviewing trends for Olsen-P and Colwell-P, CaCl₂-P analysis of P_{fert} 0.5, and the second highest P_{init} concentration, was not deemed necessary (na).

Absolute change in extractable P concentrations according to P_{init} concentration, P_{fert} and soil

Calcium chloride-P, Olsen-P, and Colwell-P concentrations significantly ($P < 0.001$) changed over the monitoring period of up to three to four and a half years. Strong relationships existed between P_{init} and final P concentrations ($P < 0.001$; $r^2 = 78.3, 82.8$ and 71.5 for $CaCl_2$ -P, Olsen-P and Colwell-P, respectively), which was consistent with the findings of Dodd *et al.*, (2012). The mean absolute decreases over the entire monitoring period across all soils, P_{init} concentrations and P_{fert} rates were $-4.5, -7.8$ and -8.4 mg/kg for $CaCl_2$ -P, Olsen-P and Colwell-P, respectively. Across all P_{init} concentrations and soils, and when no P_{fert} was applied, the mean decrease was larger at -4.6 mg/kg (ranging from -2.6 to -7.9 mg/kg according to P_{init}), -10.8 mg/kg (-3.3 to -23.7 mg/kg) and -20.4 mg/kg (-0.2 to -51.5 mg/kg), for $CaCl_2$ -P, Olsen-P, and Colwell-P, respectively. These decreases in Olsen-P and Colwell-P suggest that, for the majority of the soils with concentrations well above agronomic optimum, i.e. P_{init} Categories 3 and 4 for most soils, P fertiliser can be withheld for many more years without impacting on pasture production. The exceptions being soils with P_{init} concentrations just above agronomic optimum, for example, Soil 3 with an initial Olsen-P of 20.1 mg/kg and a decrease of -7.7 mg/kg over the monitoring period (Figure 2.2). Soil 3 measured the greatest decrease in $CaCl_2$ -P over the monitoring period (-15.7 mg/kg), followed by Soil 6 (-10.0 mg/kg), Soil 4 (-2.0 mg/kg), and Soils 1, 2 and 5 ($-0.1, -0.4$, and -0.2 , respectively). For Olsen-P, the greatest decrease occurred for Soils 1, 2, 3 and 7 ($-9.4, -12.0, -9.7$ and -11.7 mg/kg, respectively). While for Colwell-P the greatest decreases occurred for Soils 1, 2 and 7 ($-31.2, -20.4$ and -28.5 mg/kg, respectively).

When mean decreases across all soils, P_{init} concentrations, and P_{fert} rates were expressed as a percentage, $CaCl_2$ -P declined the greatest (-57%), followed by Olsen-P (-25%), and Colwell-P (-12%). Dodd *et al.*, (2012) also reported mean $CaCl_2$ -P decreased more rapidly than Olsen-P. Thus, by reducing or withholding P fertiliser, the potential for environmental loss decreased faster than the potential to supply P to plants. This is an important finding. Clearly, P readily available in the soil solution ($CaCl_2$ extractable) is decreasing most rapidly, due to this P pool being weakly sorbed but still extractable by the Olsen and Colwell methods.

Exactly how long it will take before extractable soil P concentrations to reach agronomic optimum is not known, although the current study suggests it will take more than three years. Dodd *et al.*, (2012) reported that the time for Olsen-P concentrations to decrease to agronomic optimum was shorter than the time required for water extractable P concentrations to decrease to their environmental threshold for several longer-term trials (7, 16, 21 and 26 years). This suggests that even when excessive soil P concentrations are reduced to agronomic optimum, some soils may still pose a risk of environmental P loss. Since half of the soils studied by Dodd *et al.*, (2012) had low P retention capacities, we suggest soils with greater sorption capacities would be able to support optimum pasture production without P losses being above the environmental threshold. Further monitoring would assist our understanding of fractional changes in soil P for a range of soils, P_{init} concentrations, and on-going P_{fert} rates.

Influence of soil properties and P export on P concentration change

There were significant ($P < 0.05$) relationships between total-P, OxAI, OxF_e, Po, organic-C, PSC and PBI of the characterised soils, and the change in CaCl₂-P, Olsen-P and Colwell-P, and between soil texture (i.e. sand, silt and clay content) and change in CaCl₂-P. Table 2.4 shows regressions where r^2 values were at least 30%. Incorporation of more soil characteristics into the regression did not increase r^2 values sufficiently to warrant their inclusion in the model. Desorption kinetics studies have shown OxAI and OxF_e affect decreases in P (Lookman *et al.*, 1995; McDowell and Sharpley, 2003). Burkitt *et al.*, (2002a) reported that multiple linear regressions involving PSC and either organic-C, which affects sorption site availability, or exchangeable hydrogen, which influences soil charge, were useful measures of predicting decreases in soil P. Herlihy *et al.*, (2004) found no effect of soil texture but suggested the lower buffering of limestone compared to non-limestone soils contributed to an observed difference in extractable soil P decreases. Using the same dataset as Herlihy *et al.*, (2004), Schulte *et al.*, (2010) reported parent material to have a marginally insignificant ($P = 0.052$) influence on the parameter that described the relative slope of decline. Over the long-term, decreases would be expected to be slower the higher a soil's PBI. This is because high PBI soils tend to have greater total-P concentrations, due to more P inputs being required to achieve a target extractable P concentration, and due to their greater resistance to release sorbed P i.e. greater buffering. The small r^2 values of the current study for the majority of the regressions mean that little variation in extractable P change was explained by the individual soil characteristics. This suggests that soil properties are important influencers of P change, however, other variables such as P_{init} concentrations had a larger influence, in this, and other studies. Experiments with a wide range of soils replicated under controlled conditions are required in order to shed more light on the role of soil properties on P decreases.

Although P can be taken up in quantities excess to plant requirement as soil available P concentrations increase (Burkitt *et al.*, 2010a), the majority of the P in excess of animal requirements is returned in animal excreta (Haynes and Williams, 1993). Phosphorus exports were estimated to be between 2.9 and 12.3 kg/ha.yr, according to soil and soil P concentration, and were not expected to have a large influence on the decrease in extractable soil P concentrations (McCollum, 1991) when compared to other factors such as P_{init} concentration and on-going P_{fert} . The small change in soil extractable P measured in the control plots over time suggests that P removal from these plots was low. However, some of the P removed from the control plots, and indeed other plots, may have been replaced through soil Po and OM mineralisation and solubilisation, P desorption, and P transfer from higher concentrated plots or paddocks through manure. If P was exported through cutting and carrying the pasture from the plots, greater decreases in extractable soil P as soil P concentrations increase, until a maximum P export potential is reached, may result. The maximum P export potential would be limited by the maximum pasture production (i.e. agronomic optimum), and potentially a maximum luxury uptake of P by plants (i.e. maximum plant P concentration). Interestingly, Burkitt *et al.* (2010a) reported a linear relationship between soil Olsen-P and pasture P concentration (%) for soils similar to Soils 1 ($r^2 = 0.50$) and 6 ($r^2 = 0.41$) of the current study. However, the Olsen-P concentrations plotted by Burkitt *et al.* (2010a) were within the agronomic optimum range for the soil similar to Soil 1, and from ~44 to

~55 mg/kg for the soil similar to Soil 6, thus, did not reflect the extreme Olsen-P concentrations of the current study.

Table 2.4. Linear regressions between soil characteristics and change in $\text{CaCl}_2\text{-P}$ concentrations when r^2 was greater than 30%

Explanatory variates	r^2 %	P value
OxAl	31	<0.001
Organic-C	31	<0.001
Sand	54	<0.001
Silt	59	<0.001
Clay	36	<0.001
PBI	34	<0.001

CONCLUSION

This study has successfully monitored decreases in extractable soil P concentrations that would be expected for commercial dairy pastures where Pi fertiliser has been the primary P source. It incorporated comparable P_{init} concentrations, on-going P_{fert} rates, and soils to those intensively grazed in Australasia. Greater decreases occurred the higher the P_{init} concentration and the lower the on-going P_{fert} . After three to four and a half years of withholding P fertiliser, P_{init} concentrations which were well above agronomic optimum remained above this level, thus, no decreases in pasture production would be expected. Regular soil analysis is recommended to ensure concentrations do not decrease below agronomic optimum if P fertiliser application is withheld for a period greater than that of this study. The more rapid decrease in $CaCl_2$ -P than agronomic-P suggests environmental risk is likely to decrease more rapidly while soil P concentrations are being utilised. Further study of a wide range of replicated soils under controlled conditions is required to identify which soil properties most greatly influence extractable soil P decreases, and whether any soil properties can be used to discern likely P decreases between soils.

3

**A MODEL TO PREDICT FINAL EXTRACTABLE SOIL PHOSPHORUS CONCENTRATION
WHEN PHOSPHORUS FERTILISER APPLICATION CEASES OR IS BELOW
MAINTENANCE**

ABSTRACT

Policy makers and land managers need better information in order to set realistic timeframes to return soils that are excessively concentrated in P to agronomic optimum and/or concentrations that pose low environmental risk. Decreases in calcium chloride-extractable P ($\text{CaCl}_2\text{-P}$), and sodium bicarbonate-extractable P (Olsen-P and Colwell-P), were modelled for six soils with contrasting P sorption properties using up to four and a half years of field monitoring data. Each soil had four initial soil P concentrations (P_{init}) each of which received four on-going rates of P fertiliser (P_{fert}) in a fully factorial experimental design (16 treatments in total). The model predicts the final P concentration by taking into account the P concentration previously measured ($\text{CaCl}_2\text{-P}$, Olsen-P or Colwell-P), time since previous measurement, and P_{fert} applied since measurement:

$$\text{Final P concentration} = (\text{previously measured P concentration} + e_p \times P_{\text{fertiliser applied}}) \exp(-d_p \times \text{years since P applied})$$

Where e is the increase in soil P for each unit of applied P and d is the decay constant representing how quickly the soil P decreased.

The greatest decreases in proportion to P_{init} occurred for $\text{CaCl}_2\text{-P}$, followed by Olsen-P, and then Colwell-P. The model tended to fit the dataset well for Olsen-P and Colwell-P, with mean overestimation of the final concentrations of 6.1 (32%) and 4.3 mg/kg (10%), respectively. Although there was less $\text{CaCl}_2\text{-P}$ data, the model successfully described it, with a mean overestimation of final $\text{CaCl}_2\text{-P}$ of 3.1 mg/kg (26%). This relatively large overestimation of final $\text{CaCl}_2\text{-P}$ was possibly due to the high $\text{CaCl}_2\text{-P}$ concentrations of the low P buffering index (PBI) soils. The model predicts an average of 14 years (ranging from 11 to 20 years) for Olsen-P concentrations of between 34 and 44 mg/kg to decrease to an agronomic optimum of 17 mg/kg. An initial Olsen-P concentration of between 55 and 96 mg/kg would take on average 32 years (ranging from 26 to 49 years). Despite soil P decreases varying according to soil, a soil related term was not incorporated into the model as there were only six soils studied. Further work with more soils is required to examine the influence of soil properties such as P sorption, on decreases in soil P. In addition, incorporation of the influence of various P exports in fodder, animal products, and/or environmental losses, on soil P decreases is also required.

INTRODUCTION

Excessive soil phosphorus (P) concentrations are a concern in parts of Europe, the United States of America and Australasia (Paulter and Sims, 2000; Sharpley *et al.*, 2001; Gourley *et al.*, 2010; Qiu, 2010). Soils with more P than is needed for agronomic purposes can result in elevated concentrations of P in runoff (Sharpley and Rekolainen, 1997; Burkitt *et al.*, 2010b), which can contribute to eutrophication of waterways (Carpenter *et al.*, 1998). These excessive P concentrations are a result of P inputs through fertiliser and livestock feeds and manures exceeding P exports in produce. Some land managers still apply P fertiliser when soil P concentrations are above agronomic optimum, despite being aware of the economic and environmental risks, especially in intensive pasture industries (Nicon Rural Services, 2010). This approach is used as a form of risk management to ensure that soil P does not suddenly decrease below the agronomic optimum and result in a subsequent decrease in pasture production. However, it results in inefficient use of P fertiliser, a finite resource which is in increasing world demand (Smil, 2000; Condon *et al.*, 2005).

In response to increasing P concentrations in some water resources, policies have been implemented in some countries to prevent further increases in soil P concentrations that are above agronomic optimum (European Parliament and Council, 2000). For example, in the Netherlands, application of P fertiliser will be increasingly restricted until 2015 when application rates will not be allowed to exceed P removal rates (van der Salm *et al.*, 2009) without financial penalty to the land manager. In order for land managers and policy makers to better understand how to manage soil P so as to decrease excessive concentrations without risking production losses, models of the changes in soil P under various scenarios are needed.

A number of researchers have described an exponential decrease in extractable soil P after P fertiliser application has ceased (McCollum, 1991; Paris *et al.*, 2004; van der Salm *et al.*, 2009). A number of mechanistic (Russell, 1977) and descriptive (Cox *et al.*, 1981; Schulte *et al.*, 2010; Dodd *et al.*, 2012) models have been devised to model soil P decline. Schulte *et al.*, (2010) and Dodd *et al.*, (2012) developed models across a range of initial P (P_{init}) concentrations and soils, with Schulte *et al.*, (2010) also presenting a number of negative P-balance scenarios. However, these models did not include the influence of different on-going P fertiliser (P_{fert}) rates on decreases in extractable soil P, a practice which commonly occurs on intensive pasture soils and agricultural enterprises more generally. In addition, models have typically been based on a single soil, or on a group of soils, that encompass a relatively small range in sorption capacities. Chapter 2 described changes in extractable soil P in a range of field soils which each contained a range of P_{init} concentrations and on-going P_{fert} rates. In the current paper, we use a Bayesian statistical framework to describe the changes in environmental P ($CaCl_2$ -P) (Houba *et al.*, 2000) and agronomic P (Olsen-P and Colwell-P) (Olsen *et al.*, 1954; Colwell, 1963) datasets from the same field study. We use a Bayesian approach to allow for uncertainty in measurement and parameters to be incorporated in a natural way through the appropriate prior specification. Bayesian methods also allow complex models to be more easily constructed (Brooks, 2003). Our aim was to develop a model to predict the final extractable soil P concentration after a specified time period for various soil and P fertiliser scenarios. This model could be used by policy makers and land managers to assist their decision making and to

set realistic timeframes to return soils that are excessively concentrated in P to agronomic optimum concentrations and/or concentrations that pose low environmental risk.

MATERIALS AND METHODS

Site management and soil characterisation

The materials and methods employed to obtain the dataset used to develop the Bayesian model were presented in Chapter 2. Unique to this study were the measurement of both unadjusted P buffering index (PBI) (Burkitt *et al.*, 2008) and the amount of P sorbed after addition of 1000 mg P/kg (Ps_{1000}) for the initial and final soil samples for all treatments. Both PBI and Ps_{1000} were undertaken using the PBI method (Burkitt *et al.*, 2008; Rayment and Lyons, 2011). Briefly, 1 g of soil was shaken for 17 h in 0.01 M $CaCl_2$ with an addition of 1000 mg P/kg soil (Burkitt *et al.*, 2008). The difference between the added P and the final P concentration in the equilibrating solution was the amount of P sorbed (Ps_{1000}), with PBI calculated as P sorbed (mg/kg) / [final P solution (mg/L)^{0.41}].

Bayesian statistics

Bayesian inference is the process of fitting a probability model to a set of data and summarising the results via probability distributions on the parameters of the model. In a Bayesian model, the parameters are considered to be uncertain and are therefore represented by probability distributions, known as prior distributions, or priors. These are combined with the model likelihood to obtain posterior distributions that provide their most probable values given the data and modeling assumptions (Berger, 1993). The posterior distributions are summarised using summary statistics. Using a Bayesian framework allows the inclusion of uncertainty in parameters and models, the probabilistic representation of the model outcomes, as well as conveniently constructing very complex models.

Model construction

Due to the larger decreases the greater the P concentration reported over time in Chapter 2, we developed an exponential decay model. The model was based on (1) the P_{init} concentrations, and (2) the amount of P added as on-going P_{fert} , with each plot being repeatedly measured over time. Although the treatments (i.e. P_{init} and P_{fert}) were used in constructing data summaries, they were not distinct within the model. Time was measured in 12 month intervals for $CaCl_2$ -P and 6 month intervals for Olsen-P and Colwell-P. Thus, the $CaCl_2$ -P parameter estimates were based on less than half the data of Olsen-P and Colwell-P. All sixteen treatments were measured for Olsen-P and Colwell-P, while $CaCl_2$ -P was measured from nine selected treatments; the two lowest and the highest P_{init} concentrations receiving either zero or one of the two highest P_{fert} rates. The model was fitted using Markov Chain Monte Carlo techniques by means of JAGS software, version 3.1, using 500 000 iterations, a burn-in of 250 000, and thinning every 250 iterations.

The model used Equation 3.1 to reflect the changes in P that were offset by P_{fert} application. In Equation 3.1 $Y_{p,t}$ was the soil P concentration at time (t) for each treatment plot (p); $Y_{p,t-1}$ represented the previous soil P concentration; $A_{p,t-1}$ was the amount of P previously applied (divided by 1000 for numerical convenience); S represented the time in years since measurement of the previous soil P concentration; and e_p and d_p were parameters which were estimated and were required to be positive, with e_p representing the increase in extractable soil P for each unit of applied P, and d_p representing a decay constant that reflects how quickly the extractable soil P decreases i.e. moves from the labile to unavailable pools, is removed in product, or otherwise lost from the soils.

$$Y_{p,t} = (Y_{p,t-1} + e_p A_{p,t-1}) \exp(-d_p S) \quad (3.1)$$

Final P concentration = (previously measured P concentration + $e_p \times$ P fertiliser applied) $\exp(-d_p \times$ years since P applied)

The model is universal for all three P measures (mg/kg), P fertiliser applied is expressed as kg P/ha, and estimated soil specific e and d values are listed in Table 3.3. The observed final soil P concentrations for each of the measures were denoted by $P_{p,b}$ which was assumed to be normally distributed, with means given by the modelled value $Y_{p,b}$ and with reciprocal variance τ (Equation 3.2).

$$P_{p,t} \sim N(Y_{p,t}, \tau) \quad (3.2)$$

Prior distributions were assigned to the parameters of the Bayesian model (Table 3.1). Vague priors were used so that inferences were informed by the data rather than the prior parameters. Vague priors make minimal assumptions so that the results depend on the data and not on the assumptions made by the priors. The parameters e_p and d_p were assumed to be normally distributed, each with soil specific means, e_s and d_s , where the subscripts p and s are indices for plot and soil. The e_s and d_s were assumed to be normally distributed with common global means, e_0 and d_0 , respectively. Thus, plot parameters could vary around their soil means, which themselves were distributed around a global mean. The normal distributions were truncated on the left at zero so that the parameters remained positive (Table 3.1).

Using the model, the time required for P_{init} to decrease to agronomic optimum [defined as 17 mg/kg for Olsen-P (Gourley *et al.*, 2007) and as 55, 40, 23, 29, 55 and 29 mg/kg for Soils 1 to 6, respectively, for Colwell-P (Gourley *et al.*, 2007)] or an environmental threshold (defined as ≤ 0.25 mg/kg for CaCl_2 -P) was calculated. Uncertainties in P_{init} were calculated on one standard deviation from the mean.

Table 3.1. Assignment of priors to parameters e_p and d_p for a Bayesian model of soil P concentration change across six soils, each with a range of P_{init} concentrations and P_{ferts}

The observation precision, τ , in Equation 3.2 and all precisions in this table ($\tau_{e_s}, \tau_{e_p}, \tau_{e_0}, \tau_{d_p}, \tau_{d_s}, \tau_{d_0}$) were assigned vague gamma priors with shape and rate parameters set to 0.01; e.g. $\tau_{e_s} \sim Ga(0.01, 0.01)$. The initial predicted value; $Y_{p,1}$ was unlike later predictions in that it was assumed to not be subject to earlier P applications, but informed only by the first observed P value, and was assigned a uniform distribution so that any value between the upper and lower limits was equally probable.

P_{fert} constant	Decay constant
$e_p = N\left(e_s, \tau_{e_p}\right)$	$d_p = N\left(d_s, \tau_{d_p}\right)$
$e_s = N\left(e_0, \tau_{e_s}\right)$	$d_s = N\left(d_0, \tau_{d_s}\right)$
$e_0 = N\left(0.1, \tau_{e_0}\right)$	$d_0 = N\left(0.1, \tau_{d_0}\right)$
$Y_{p,1} \sim U(0, 1000)$	

RESULTS AND DISCUSSION

Predicted versus observed final $CaCl_2$ -, Olsen- and Colwell-P concentrations

Posterior predictions and observed soil $CaCl_2$ -P, Olsen-P and Colwell-P concentrations (Figure 3.1) were highly correlated ($r^2 > 0.85$), suggesting that the curves of the model fitted the dataset well for all three P measures. Final Olsen-P and Colwell-P concentrations, which were initially approximately twice agronomic optimum or lower, were the most accurately predicted. The precision of the model for P concentrations which were initially near agronomic optimum should be reassuring to land managers and policy makers as it limits the chances of soil P concentrations decreasing below agronomic optimum faster than predicted. However, the large range in soil P concentrations of the dataset resulted in modelled values diverging from observed values as Olsen-P and Colwell-P concentrations increased (Figure 3.1). This divergence meant that the model overestimated the final P concentration i.e. the greater the P_{init} concentration, the greater the predicted final P concentration was compared to the actual final P concentration (Figure 3.1). This may have been the result of the smaller population of data at high P_{init} concentrations, for example, Soil 3 did not contain high Olsen and Colwell P_{init} concentrations.

Since the dataset used to develop this model was sourced from grazed field soils, some decreases in extractable soil P would be the result of P being exported in grazing animal products (estimated to be between 2.9 and 12.3 kg P/ha.yr), and environmental losses. These estimated exports changed according to soil and P_{init} concentration, as would any environmental losses which may occur. The current model includes these exports as contributing to the decreases in extractable soil P concentrations. Further population of the model with

data which compares decreases in extractable soil P and various rates of P export from a soil is required, and may lead to incorporation of a P export term. However, the decrease in extractable soil P is driven by readily extractable P being sorbed by the soil (Barrow, 1980), and conversion to forms not CaCl_2 or bicarbonate extractable, i.e. organic P (Po) or recalcitrant inorganic-P (Pi).

It could be argued that our model was predicting decreases in the effectiveness of the capital fertiliser applied at trial site establishment. As a result, the final P concentrations we observed may be expected to be lower than those in soils where similarly high P_{init} concentrations were established over a longer period. However, if that were the case, our model would more closely represent the higher final P concentrations since the model overestimated final P mainly for high P_{init} soils. Irrespective of this, greater decreases in soil extractable P have been reported for high P_{init} concentrations, whether built-up over a short or long period (McCollum, 1991). Indeed, Mehlich-1 P_{init} concentrations, which were achieved through a single application of P fertiliser or progressively over eight years of P fertiliser applications, had loss constants of -0.097 ($r^2=0.89$) and -0.073 ($r^2=0.81$), respectively, for initial Mehlich-1 P of 100 g m^{-3} , -0.068 ($r^2=0.73$) and -0.080 ($r^2=0.72$) for initial values of $40\text{-}60 \text{ g m}^{-3}$, and -0.047 ($r^2=0.52$) and -0.048 ($r^2=0.41$) for initial values of $20\text{-}30 \text{ g m}^{-3}$ (McCollum, 1991). When averaged across all soils P_{init} concentrations and P_{fert} , our model overestimated final Olsen-P and Colwell-P concentrations by 6.1 mg/kg (32%) and 4.3 mg/kg (10%), respectively (Table 3.1). The overestimation for final Colwell-P was within analytical error suggesting that the model was most successful at predicting final Colwell-P concentrations. Still, the overestimation for Olsen-P was small considering the range in P_{init} concentrations and soils. The Olsen-P method generally extracts soluble orthophosphate P, including P that can be rapidly desorbed from soil particles (Coventry *et al.*, 2001). The longer extraction time for the Colwell-P method includes orthophosphate as well as molybdate-reactive non-orthophosphate P compounds (Coventry *et al.*, 2001). Thus, in addition to the background P exports, the model well reflects the movement of P from readily available to less available forms, and to less a degree the rapid and reversible sorption reactions which would have influenced the decreases in CaCl_2 -P and Olsen-P concentrations.

Similar to Olsen-P and Colwell-P, the divergence of the predicted CaCl_2 -P concentrations from the observed concentrations was greater as P_{init} concentrations increased (Figure 3.1). The greater a soil's CaCl_2 -P concentration, the greater the amount of P available to move to less available P pools through processes such as sorption and precipitation, to be removed in animal products, and to be lost to the surrounding environment. The model overestimated average final CaCl_2 -P concentrations by 3.07 mg/kg (26%). The final P concentrations for Soils 3 and 6, with the highest CaCl_2 -P concentrations and lowest PBIs were overestimated by a mean of 9.1 mg/kg (140%) (Table 3.2). Whilst these may be large overestimations when compared to the environmental CaCl_2 -P threshold i.e. $\leq 0.25 \text{ mg/kg}$ (0.05 mg/L), they were not when compared to the initial CaCl_2 -P concentration range of the dataset. We hypothesise that the extremely high CaCl_2 -P concentrations measured from Soils 3 and 6, and the fewer data available for CaCl_2 -P, contributed to the overestimation. The extreme CaCl_2 -P concentrations of Soils 3 and 6 appear to be due to the soil's low PBIs. Soil 3 (Podosol) and 6 (Hydrosol) contained the lowest oxalate-extractable iron and aluminium contents, lowest clay and highest sand contents, and some of the highest organic carbon contents, of all the soils.

Phosphorus movement from the surface 10 cm, and conversion to forms not $\text{CaCl}_2\text{-P}$ extractable, may have contributed more to P decreases than sorption processes for Soils 3 and 6. Indeed, the greater a $\text{CaCl}_2\text{-P}$ concentration is, the greater is the risk of environmental loss. This is evident by the modelled final P concentrations being much closer to the observed final P concentrations for the very low PBI Soil 4 which had lower initial $\text{CaCl}_2\text{-P}$ concentrations than the extremely low and very low PBI Soils 3 and 6, respectively (Table 3.2). Final $\text{CaCl}_2\text{-P}$ concentrations for Soils 1, 2 and 5, which had much lower initial $\text{CaCl}_2\text{-P}$ concentrations, and higher PBIs, were underestimated by an average of -0.13 mg/kg (-53%).

Table 3.2. Absolute and percentage overestimation (positive) and underestimation (negative) of model prediction compared to the observed final concentrations for each P measure and soil, and across all soils

Soil	$\text{CaCl}_2\text{-P}$	$\text{CaCl}_2\text{-P} \%$	Olsen-P	Olsen-P %	Colwell-P	Colwell-P %
1	-0.15	-66	7.7	20	25.6	7
2	-0.11	-39	9.6	25	17.1	9
3	10.89	175	7.7	110	4.1	29
4	0.68	36	2.4	<1	-6.3	-10
5	-0.13	-54	-0.7	-4	-37.4	-20
6	7.24	104	9.3	39	22.8	44
All	3.07	26	6.1	32	4.3	10

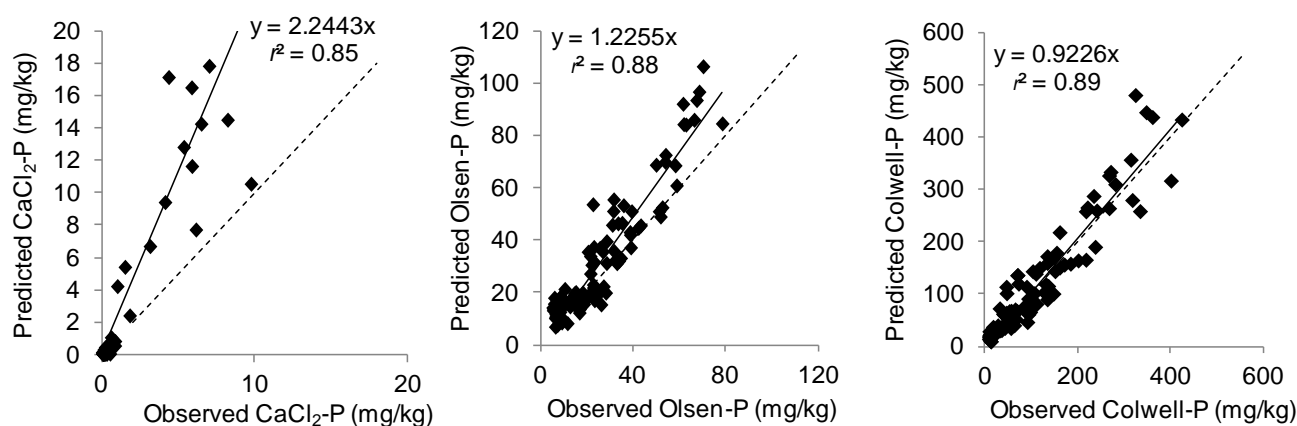


Figure 3.1. Relationship between observed and predicted final $\text{CaCl}_2\text{-P}$, Olsen-P and Colwell-P concentrations of the surface 100 mm for six Australian soils and all P_{init} concentrations and P_{ferts} . Solid line is the fitted regression and dashed line represents $x=y$. Points above the dashed line represent overestimation of final P concentration, while points below represent underestimation of final P concentration.

Influence of P_{fert} on the modelled final P concentration

It is important to examine the influence of P_{fert} on the modelled final P concentration because it is a variable that the land manager can control. Whilst some land managers would rather not omit P_{fert} inputs altogether, soil P concentrations may still decrease if the P_{fert} applied is less than that required to maintain soil P concentrations. There was a range in e_s values (increase in extractable soil P concentration for each unit of applied P) across the soils, where smaller e_s values indicated soils which were less responsive to P_{fert} when presented in isolation from the soil effect (Table 3.3). Changes in P concentrations of Soils 3 and 6 were the least sensitive to P_{fert} when extracted with CaCl_2 (Table 3.3); contrasting with current assumptions that relatively low rates of P fertiliser are required to increase fertility of low PBI soils (Burkitt *et al.*, 2001). This may in part be due to the on-going P_{fert} moving beyond the surface 10 cm of these – very low P sorption capacity, coarse textured – soils which receive high annual rainfall (~1100 mm). Indeed, difficulty was encountered in increasing agronomic extractable soil P concentrations for the extremely low PBI Soil 3. Despite application of 500 kg P/ha, split over 12 months, Olsen-P of Soil 3 only increased from 13 to 19 mg/kg (Chapters 2 and 6). Alternatively, the high initial CaCl_2 -P concentrations of these soils, and conversion of the applied P_{fert} to forms unextractable by CaCl_2 , such as Po through incorporation into the plant biomass and microbial population, may have also contributed to this low sensitivity to the applied P_{fert} . Olsen-P and Colwell-P concentrations of Soils 3 and 6 were more sensitive to P_{fert} than Soils 1 and 2 of higher PBI, which were the least sensitive (Table 3.3). This suggests that Soils 3 and 6 had some capacity to weakly sorb P which was not CaCl_2 -P extractable, and/or desorb molybdate-reactive non-orthophosphate P compounds. It is not known why changes in Olsen-P and Colwell-P in Soils 1 and 2 were the least sensitive to P_{fert} when Soils 4 and 5, which had greater PBIs, were the most sensitive to P_{fert} for all three extracts.

Influence of soil on the modelled final P concentration

Despite soil PBI being an important factor in determining the appropriate P fertiliser rate to increase soil P concentrations, few studies have modelled P decreases across a range of soils. Kerridge *et al.*, (1990) reported that the negligible P sorption capacity of the soils they studied meant that a 'soil' term did not need to be included in the model they used. However, the dataset that was used to construct the current model showed that extractable P concentration decreases were variable according to soil (Chapter 2).

Despite absolute decreases in CaCl_2 -P concentrations being the largest, Soils 3 and 6 had the lowest d_s values (decay constant that reflects how quickly the extractable soil P decreases). This suggests that the CaCl_2 -P concentrations of the two lowest PBI soils decreased more gradually than those of higher PBI soils (Figure 3.2 and Table 3.3). This is in agreement with that reported by Burkitt *et al.*, (2002a) that high PBI soils are continuously sorbing P and as a result speed up decreases in readily available P when compared to medium PBI soils. While the CaCl_2 -P concentrations would have decreased through continuous P sorption for the higher PBI soils, the lower PBIs of Soils 3 and 6 would suggest little sorption would have taken place. In support of little sorption occurring, Olsen-P (intensity) and Colwell-P (quantity) concentrations decreased fastest (highest d values) for Soils 3 and 6 (Figure 3.2 and Table 3.3), despite having some of the lowest P_{init}

concentrations. It is thought that vertical movement of P beyond the soil sampling depth, and conversion to forms not directly extractable, were the two most likely pathways responsible for the decreases in extractable P for Soils 3 and 6. In comparison, the capacity of the soils with higher PBI to buffer changes in soil solution P may have been responsible for their more gradual decrease in Olsen-P and Colwell-P concentrations. Excluding Soils 3 and 6, the greater the PBI, the more gradual was the decrease in extractable soil P concentrations.

The hypothetical inability of Soils 3 and 6 to retain large concentrations of extractable Pi is in contrast to their extreme $\text{CaCl}_2\text{-P}$ concentrations. Since the $\text{CaCl}_2\text{-P}$ concentrations of Soils 3 and 6 were similar to the Olsen-P concentrations, it is possible that their high organic carbon content may have led to greater hydrolysis of Po to readily available P. The acidic molybdate-solution may cause hydrolysis of Po so that the molybdate-blue colour reaction of Murphy and Riley (1962) does not exclusively represent Pi (Haygarth and Sharpley, 2000). Thus, it is possible that the gradual decreases in $\text{CaCl}_2\text{-P}$ concentrations were partly due to decreases in Po.

We have successfully modelled decreases across a range of soils, and identified varying decreases according to P extraction, soil type, and PBI. However, we suggest P decreases of more soils are needed before a term based on PBI can be incorporated into our model. If such a soil term could be incorporated we suggest the accuracy of the predictions would increase further.

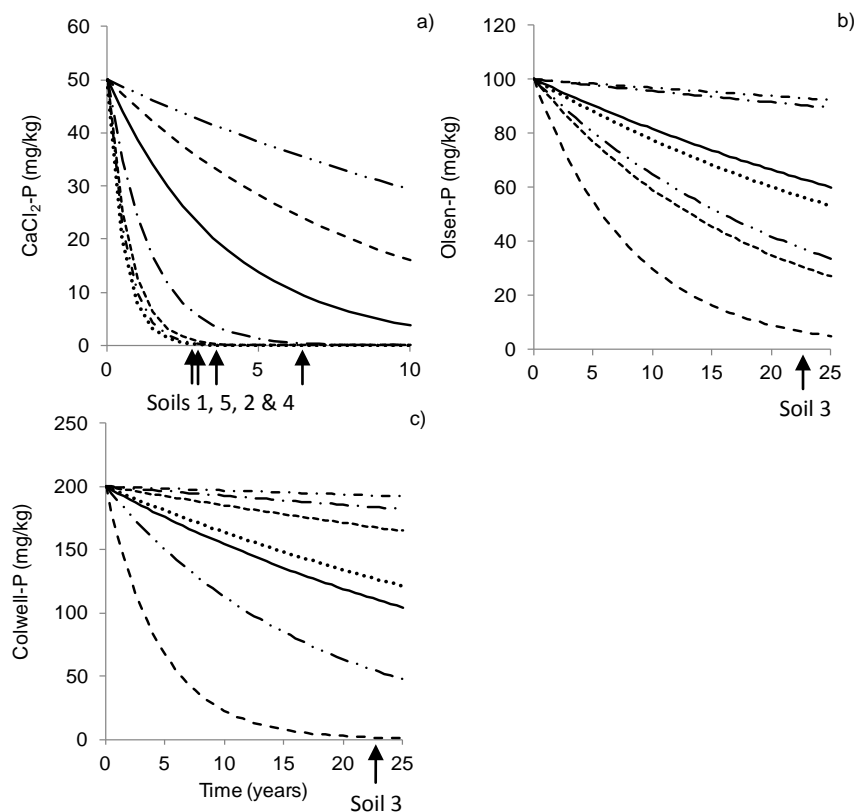


Figure 3.2. Predicted a) $\text{CaCl}_2\text{-P}$, b) Olsen-P and c) Colwell-P generic curves with zero P_{fert} (solid lines) which used the global parameters across all soils (d_0); and for Soil 1 (...), Soil 2 (---), Soil 3 (— —), Soil 4 (— · —), Soil 5 (· · ·), and Soil 6 (— · · —), using soil parameters (d_s). Labelled arrows indicate the estimated time required for soils to reach environmental and agronomic thresholds. Note x- and y-axes are differently scaled.

Table 3.3. The $\text{CaCl}_2\text{-P}$, Olsen-P and Colwell-P posterior statistics of d and e in isolation from each other, on a global (d_0 and e_0) and soil (d_s and e_s) level

e represents the increase in extractable soil P for each unit of applied P, and d represents a decay constant that reflects how quickly the extractable soil P decreases. The larger the number, the more sensitive the extraction is to changes in soil P

Soil	Mean d	SD d	Mean e	SD e
<i>CaCl₂-P</i>				
Global	0.3769	0.3725	0.6005	0.7713
1	2.1332	1.1271	1.0555	1.2675
2	1.6377	0.9493	1.1279	1.3648
3	0.1146	0.0604	0.9510	1.0540
4	0.7471	0.1890	1.1756	1.4114
5	1.9853	1.2190	1.1683	1.5647
6	0.0611	0.0455	0.8212	0.8336
<i>Olsen-P</i>				
Global	0.0271	0.0241	0.2533	0.3029
1	0.0260	0.0140	0.3237	0.3038
2	0.0515	0.0142	0.3405	0.3013
3	0.1215	0.0175	0.4849	0.5905
4	0.0058	0.0052	0.5035	0.6312
5	0.0043	0.0040	0.5975	0.7944
6	0.0432	0.0130	0.4059	0.4167
<i>Colwell-P</i>				
Global	0.0355	0.0323	5.4581	10.1002
1	0.0200	0.0100	3.0582	2.6847
2	0.0094	0.0074	4.7165	4.2606
3	0.2239	0.0574	33.5996	22.1170
4	0.0050	0.0043	38.1874	14.6719
5	0.0022	0.0021	127.6211	18.0604
6	0.0569	0.0121	4.7348	4.1758

Influence of P_{fert} and soil on modelled P decrease

The magnitude of the effect of P_{fert} was less than soil since the decreases in P were more variable between soils than between rates of P_{fert} (Table 3.3). This may in part be due to different animal product exports (2.9 to 12.3 kg P/ha.yr according to soil and soil P concentration), and potential for surface runoff of P according to soil, from the trial sites which populated our model. Schulte *et al.* (2010) reported that their large P deficit due to P export in fodder removed from their trial sites was the driver of P decreases (contributing 63%) for eight moderate to low PBI soils. Despite this, and the small range in PBI of the soils studied by Schulte *et al.* (2010), they reported a relationship between Morgan-P decreases and parent material of the individual soils that was marginally insignificant ($P=0.052$). The greater influence of soil than P_{fert} in the current study was thought to be due to the large range of soils examined and supports the need to investigate P decreases across a larger number of soils which cover a wide range of P sorption properties.

Since there was one experimental site per soil, each of the site-level parameters corresponds to a soil type with associated properties such as PBI. However, a highly significant ($P < 0.001$; $r^2 = 0.95$) linear relationship existed between Ps_{1000} and the d_p parameter for $CaCl_2$ -P. Due to the PBI scale not being linear; i.e. a PBI of 400 does not have double the sorption capacity of a PBI of 200, there was a highly significant ($P < 0.001$) logarithmic relationship between PBI and the d_p parameter for $CaCl_2$ -P ($r^2 = 0.97$). There was also a significant ($P < 0.05$) linear relationship between d_p for Olsen-P and Colwell-P and Ps_{1000} ($r^2 = 0.24$ and 0.38 , respectively). However, the polynomial relationship for d_p of Olsen-P was stronger ($r^2 = 0.40$) than the linear relationship, as was the exponential relationship for Colwell-P d_p ($r^2 = 0.57$). Although the parameters for this model are soil specific, information on their magnitude and interrelationship will assist in estimating decreases for other soils. For example, changes in P concentrations of Podosol and Hydrosol soils which are coarse textured, contain high organic matter contents, and low to extremely low PBIs due to low clay and oxalate-aluminium and oxalate-iron contents, would be expected to be different to medium and high PBI soils.

Time until environmental and agronomic optimum P concentrations are reached

The model estimated that for the majority of the soils, it would take up to 2.7 years for $CaCl_2$ -P concentrations of ≤ 1.71 mg/kg ($CaCl_2$ -P concentrations of Soils 1, 2, 4 and 5) to decrease to an environmentally acceptable level of ≤ 0.25 mg/kg (0.05 mg/L) (Table 3.4). This is a shorter period of time than that reported by Dodd *et al.* (2012) of 22-44 years for surface 75 mm water extractable-P (WEP) concentrations of 0.039-0.141 mg/L to decrease to an environmentally acceptable level of 0.02 mg/L (0.10 mg/kg). When Dodd *et al.*, (2012) reported WEP and $CaCl_2$ -P concentrations were plotted, there was no relationship between the two measures. This explains why Dodd *et al.*, (2012) did not report exponential decreases in $CaCl_2$ -P for three of their four sites, while they did report exponential decreases in WEP for three sites.

Dodd *et al.*, (2012) estimated that WEP concentrations of the two soils with the greatest P retentions (PR) would take twice as long to reach the target concentration than a soil with a lower PR. We converted the PR (%) reported by Dodd *et al.*, (2012) to approximate PBI values using data from Burkitt *et al.*, (2002b) to conclude that the PBI range was approximately 90-600 for their lowest P fertiliser treated soils. Based on this conversion, the PBI's of two of Dodd *et al.*, (2012) soils were less than 150, as were three of our soils. When we modelled our two lowest PBI soils the model estimated it would take on average 20 years, ranging from 3 to 35 years, for $CaCl_2$ -P concentrations to decrease from between 19 and 28 mg/kg for Soil 3, and on average 34 years, ranging from 17 to 41 years, to decrease from between 10 and 29 mg/kg for Soil 6; to ≤ 0.25 mg/kg (Table 3.4). For our $CaCl_2$ -P concentrations to decrease to Dodd *et al.*, (2012) WEP threshold of 0.10 mg/kg, our model predicted it would take 37 years, ranging from 4 to 53 years for Soil 3, and 47 years, ranging from 21 to 51 years, for Soil 6. While the latter mean estimates were similar to those reported by Dodd *et al.*, (2012) for WEP, in contrast to Dodd *et al.* (2012), our lowest PBI soils took longer to decrease than higher PBI soils. This may be due to our initial $CaCl_2$ -P concentrations, which were greatest for the lowest PBI soils, were much greater than Dodd *et al.*, (2012) respective $CaCl_2$ -P and WEP concentrations. This suggests that the extreme $CaCl_2$ -P concentrations of our two lowest PBI soils, and high $CaCl_2$ -P concentrations of our high PBI soils,

decreased more rapidly than those reported by Dodd *et al.*, (2012), supporting the exponential decrease we modelled for $\text{CaCl}_2\text{-P}$. Our findings are in line with simple model calculations by Schoumans and Groenendijk (2000) which showed that it would take many decades before high soil P concentrations in non-calcareous low P sorbing sandy soils would be reduced to environmentally acceptable concentrations. It is assumed that Po buffers the decreasing extractable soil P concentrations for the lowest PBI soils, in much the same way that desorption buffers decreases in higher PBI soils. This suggests that the P dynamics of organic matter accumulation and mineralisation and microbial biomass dynamics regulate extractable soil P concentrations more than do chemical sorption and precipitation reactions for the two lowest PBI soils.

An important finding of the model is that even if some soils are at or close to agronomic optimum, environmental losses can still occur. For the extremely low PBI Soil 3 and very low PBI Soil 6, $\text{CaCl}_2\text{-P}$ concentrations were above the environmental threshold when Olsen-P and Colwell-P concentrations were at or just above agronomic optima. These findings suggest the use of such soils for agricultural purposes could pose a long-term elevated risk to the environment as optimum agronomic production is unlikely to be achieved without a high risk of P loss. Similarly, for the low PBI Soil 4, Olsen-P concentrations below agronomic optima resulted in $\text{CaCl}_2\text{-P}$ concentrations above the environmental threshold. Although $\text{CaCl}_2\text{-P}$ concentrations of Soil 4 were not as great as those of Soils 3 and 6, the time taken to reach the environmental threshold was less than 6 years. However, not all soils will pose an environmental risk when soil P concentrations are at agronomic optimum. From Table 3.4, $\text{CaCl}_2\text{-P}$ concentrations of Soils 1 and 2 were not above the environmental threshold until Olsen-P concentrations were twice, and Colwell-P concentrations three to four times the agronomic optima. For Soil 5, Olsen-P and Colwell-P concentrations at or near the agronomic optima were associated with $\text{CaCl}_2\text{-P}$ concentrations close to the environmental threshold.

The current model predicts it would take on average 14 years, ranging from 11 to 20 years for Olsen-P concentrations of between 34 and 44 mg/kg to decrease to agronomic optimum of 17 mg/kg. An initial Olsen-P concentration of between 55 and 96 mg/kg would take on average 32 years, ranging from 26 to 49 years, depending on the soil (Table 3.4). In comparison, Dodd *et al.*, (2012) reported a shorter period of up to 7 years for initial Olsen-P concentrations (0-75 mm) to decrease from 51 to 25 mg/kg. This is equivalent to an initial Olsen-P of ~43 mg/kg decreasing to 22 mg/kg if sampled to 100 mm (Coad *et al.*, 2010), which our model suggests would take 25 years when using global d and e values. The time reported by Dodd *et al.*, (2012) for Olsen-P concentrations to decrease to agronomic optimum was shorter than the time they reported for WEP concentrations to decrease to the environmental threshold, despite WEP decreasing at a greater rate. This suggests that the majority of the soils they studied may have soil properties similar to Soils 3, 4 and 6 of the current study, in that they cannot be maintained at agronomic optimum without environmental loss. Colwell-P agronomic optimum varies according to soil and as such it would take on average 9 (mean range of 7 to 11 years), 47 (mean range of 39 to 59 years), and 84 years (mean range of 69 to 117 years) for initial Colwell-P concentrations of 30-90, 102-181, and 274-461 mg/kg to decrease to their respective agronomic optima of Soils 1 to 6 (Table 3.4).

Table 3.4. Modelled mean time (years) and range in time (in brackets) until various initial $\text{CaCl}_2\text{-P}$, Olsen-P and Colwell-P concentrations (mg/kg) reach environmental threshold or agronomic optima, averaged across all on-going P_{ferts} for each soil.

Note: environmental threshold for $\text{CaCl}_2\text{-P}$ was defined as <0.25 mg/kg, while agronomic optima for Olsen-P was defined as 17 mg/kg, and Colwell-P as 55, 40, 23, 29, 55 and 29 mg/kg for Soils 1 to 6, respectively.

<i>CaCl₂-P</i>		<i>Olsen-P</i>		<i>Colwell-P</i>	
Initial	Time (years)	Initial	Time (years)	Initial	Time (years)
<i>Soil 1</i>					
0.13	0	8	0	33	0
0.15	0	16	0	65	5 (4-8)
n/a	n/a	39	17 (13-24)	181	35 (27-49)
0.85	0.6 (0.4-1.2)	96	50 (33-118)	461	65 (47-135)
0.18	0	11	0	34	0
<i>Soil 2</i>					
0.21	0	19	2 (1-3)	67	19 (15-27)
n/a	n/a	44	15 (12-19)	159	47 (38-64)
1.71	1.1 (0.7-2.7)	93	19 (17-23)	335	67 (54-87)
<i>Soil 3</i>					
23.2	37 (3-156)	17	0	24	0.2 (0.2-0.3)
19.24	44 (3-181)	16	0	22	0
n/a	n/a	16	0	20	0
28.02	13 (4-16)	20	1.0 (1.0-1.3)	30	1.1 (0.9-1.5)
<i>Soil 4</i>					
0.45	0.7 (0.6-1.0)	16	0	49	22 (18-26)
0.53	0.9 (0.7-1.2)	21	8 (7-11)	65	35 (29-43)
n/a	n/a	42	32 (27-40)	139	75 (62-95)
6.96	4.4 (3.5-5.9)	73	34 (30-39)	274	96 (80-120)
<i>Soil 5</i>					
0.22	0	15	0	76	19 (16-22)
0.33	0.1 (0.06-0.3)	20	6 (5-7)	102	34 (30-39)
n/a	n/a	34	25 (22-30)	168	70 (61-81)
0.74	0.5 (0.3-1.4)	55	40 (35-47)	280	108 (94-126)
<i>Soil 6</i>					
11.22	27 (20-41)	23	11 (7-27)	47	10 (8-15)
10.33	22 (17-32)	33	18 (13-32)	73	17 (14-22)
n/a	n/a	40	15 (12-21)	90	18 (15-23)
29.51	22 (18-29)	57	15 (13-18)	134	21 (18-26)

n/a means not applicable since P_{init} was already below agronomic optimum, or was not analysed for $\text{CaCl}_2\text{-P}$.

From Table 3.4, and as mentioned above, there is a large range in predicted decreases for our model. Schulte *et al.*, (2010) reported an uncertainty in their model predictions of 3 to >20 years for Morgan-P to decrease from Index 4 to 3. Dodd *et al.* (2012) reported an estimate of 23 years could be 21 or 31 years for WEP. Our greater range in predicted decrease period may be due to the greater range of soils used. In addition, our model extrapolated our dataset more than Dodd *et al.*, (2012), who had field data for 7, 16, 21 and 26 years, depending on site, which may have contributed to our greater range in predicted decrease period. However, the advantage of our model, as opposed to a purely descriptive empirical one, is that the predictions beyond the observed data range are reasonable as long as the model assumptions are valid. We suggest that the large range in P_{init} concentrations of the dataset used for the current model contributed to these wide ranges since some of our low P_{init} concentrated soils had low prediction ranges, similar to those reported by Dodd *et al.*, (2012), with the range widening as P_{init} concentrations increased. In addition, the on-going P_{fert} would have extended some of our periods of decrease.

CONCLUSION

The model we present (Equation 3.1) predicts final soil P concentrations for a range of soils P_{init} concentrations, and on-going P_{ferts} . The model predicts the P concentration by taking into account the P concentration previously measured, time since previous measurement, and P_{fert} applied since measurement. Since decreases are slow (range from 0 to 135 years, when withholding fertiliser for environmental and economic objectives), policy makers need realistic expectations about achievable P decreases, and land managers can be reassured of the implications of withholding P fertiliser. While some soils can maintain soil Olsen-P and Colwell-P concentrations above agronomic optimum with minimal risk of P loss, other soils will exceed (sometimes many times over) the $CaCl_2$ -P environmental threshold, even if they are below agronomic optimum. While decreases in soil extractable P concentrations of the current study vary to some degree from other studies, it is unanimous that environmental losses would most likely continue whilst these decreases occur.

To achieve more rapid decreases in soil P concentrations, increases in P exports in plant and animal products would need to occur in addition to withholding P fertiliser application. To enable modeling of scenarios where various P exports occur, a P export term needs to be incorporated into the model since it is currently included only as a component of the d parameter. The range of soils studied has shown that soil with inherently very low and extremely low PBIs require different management than higher PBI soils in order to limit P losses i.e. application of different quantities and forms of P. Further work on the influence of soil properties such as PBI on extractable soil P decreases is required to refine this model.

4

**USING SOIL PHOSPHORUS CONCENTRATIONS AND DEGREE OF PHOSPHORUS
SORPTION SATURATION TO ASSESS THE RISK OF SOIL PHOSPHORUS LOSS AND SOIL
SUPPLY POTENTIAL WHEN PHOSPHORUS FERTILISER IS WITHHELD**

ABSTRACT

Soils with phosphorus (P) concentrations above that required for agronomic production (excessively concentrated) pose an unnecessary risk of P loss to surrounding waters. Omitting P fertiliser inputs to excessively concentrated soils means that plants must use existing soil P efficiently, ultimately reducing its concentration. An indication of a soil's degree of P sorption saturation (DPSS) [$DPSS_{Ox-P:\alpha_{Pmax}} = Ox-P/\alpha_{Pmax}$ (oxalate-extractable aluminium (OxAl) and iron (OxFe)) x100] in addition to P intensity and quantity concentrations, as soil P concentrations decrease, would assist in accurately predicting the reduction in the risk of P loss, as well as the soil's ability to supply P for plant uptake. Six pasture soils of contrasting P sorption capacity, each containing three initial P concentrations (P_{init}), were sampled 6 and either 36 or 48 months after receiving their final P fertiliser application. There was a significant ($P<0.001$) decrease in both intensity [calcium chloride extractable-P ($CaCl_2$ -P)] and quantity extractions [Olsen-P, Colwell-P, and Oxalate-P (Ox-P)] over this time period. Total-P did not significantly ($P>0.05$) decrease, rather, decreases in P_i were due to immobilisation into the organic-P (Po) pool, for all soils except one with an extremely low P buffering index (PBI). For the extremely low PBI soil (Soil 3), we suggest that the majority of the applied P may have moved beyond the surface 10 cm within 6 months of fertiliser application, along with desorbed and mineralised P. Soil 3's initial DPSS was 14% and decreased to 7%, compared to all the other soils which ranged from 31% (Soil 6) to 45% (Soil 4) and decreased to 22% and 39%, respectively. Despite having the lowest $DPSS_{Ox-P:\alpha_{Pmax}}$ values, the inherently very low and extremely low PBI soils had $CaCl_2$ -P concentrations which greatly exceeded the risk threshold of 0.1 mg/L (0.5 mg/kg) for environmental P loss. Therefore, soil specific critical DPSS thresholds are recommended in order to be meaningful for environmental risk. To limit the need to calculate α values for individual soils, we propose that DPSS be calculated using the amount of P sorbed after an addition of 1000 mg P/kg, as is routinely undertaken for the Australian PBI method. This measure of P sorbed could be used as a measure of P sorption capacity remaining ($PSCr_{1000}$) with Colwell-P a measure of P already sorbed, since their sum was well correlated to the sum of OxAl and OxFe. Since both PBI and Colwell-P are routinely measured in Australian laboratories, a simple calculation of DPSS, without any further cost, would be possible. However, DPSS should accompany, rather than replace, other soil P measures which can be used to estimate a soil's P supplying potential, or P loss risk. Further correlation between $CaCl_2$ -P and Australian measures of DPSS is required to set DPSS thresholds according to soil.

INTRODUCTION

A combination of increasing world phosphorus (P) demand and decreasing phosphate rock quality will inevitably result in an increase in P fertiliser costs in the future (Smil, 2000; Condrón *et al.*, 2005). Many international soils are excessively concentrated with P (Paulter and Sims, 2000; Sharpley *et al.*, 2001; Gourley *et al.*, 2010; Qiu, 2010). These excessive soil P concentrations increase the risk of P loss from soil to water. By withholding P application from excessively concentrated soils, utilisation of existing soil P could potentially occur for many years as concentrations decrease to agronomic optimum (van der Salm *et al.*, 2009; Dodd *et al.*, 2012; Chapter 3), reducing the risk of P loss for many soils. In order to understand changes in this supply potential, and reduction in environmental risk, a detailed understanding of the changes in P fractions and P sorption, when soil P concentrations decrease, is required.

The distribution of P between organic (Po) and inorganic (Pi) pools depends on total soil P concentration (Pt), soil properties, environmental conditions and management (Singh *et al.*, 2005). Solution P, often measured using a surrogate such as the 0.01 M calcium chloride (CaCl₂-P) extraction, is readily available for plant uptake and is considered an intensity (I) measure. Phosphorus fractions which supply the intensity pool are made less immediately available due to processes such as adsorption, but can contribute to estimates of P quantity in common P extractions such as Olsen-P, Colwell-P and oxalate-P (Ox-P). Although Olsen-P can be classified as an intensity measure, McDowell *et al.*, (2001a) considered that the Olsen-P versus CaCl₂-P relationship represents a quantity-intensity relationship typical of a sorption or desorption isotherm. As a soil becomes enriched or depleted in P, changes in quantity and intensity occur (Bache and Williams, 1971; Koopmans *et al.*, 2002). For example, when P fertiliser is withheld and intensity is depleted through plant uptake or loss to the surrounding environment, P from the quantity pool moves into the intensity pool, through processes such as desorption, and mineralisation and solubilisation of organic matter (OM) and Po. Thus, the relationship between quantity and intensity is important for understanding the P supplying characteristics of soil, which change with the P sorption and buffering capacities of the soil, and OM content.

Research on changes in quantity-intensity relationships induced by plant P uptake and/or soil processes such as P desorption has often involved pot or laboratory studies with plant uptake mimicked through the use of anion-exchange resin (Amer *et al.*, 1955; Barrow and Shaw, 1977), membranes impregnated with ion-exchange resin (Qian *et al.*, 1992), iron-oxide impregnated filter strips (Menon *et al.*, 1990; De Smet *et al.*, 1998), and/or repeated extraction (De Smet *et al.*, 1998). While these P sink studies have been related to soil P supplying power in pot studies (Qian *et al.*, 1992), few have examined changes in intensity and quantity properties using field soils.

Measurement of a quantity and intensity factor to fully assess a soil's potential to supply P to the soil solution for plant uptake and environmental loss has been recommended (Beauchemin and Simard, 1999; Flaten *et al.*, 2003). Degree of P sorption saturation (DPSS) is one method which integrates the quantity and intensity concepts in that it measures the P accumulated with respect to the soil's finite capacity to sorb P (Sharpley, 1995). Calculation of DPSS can involve inclusion of a scaling factor, called alpha (α), to represent the fraction of iron (Fe) and aluminium (Al) binding sites (estimated by oxalate-extractable Fe (OxFe) and Al (OxAl)

occupied by P (Equations 4.1, 4.2 and 4.3). Although 0.5 is commonly used for acid sandy soils of the Netherlands, α values have been reported to range from 0.24 to 0.68 (when not multiplied for long-term P sorption index measurement) (Paulter and Sims, 2000; Maguire *et al.*, 2001; Renneson *et al.*, 2009). Indeed, Beauchemin and Simard (1999) considered that the α value may change due to variability in physical and chemical soil characteristics, such as OM content, pH, and the particle size distribution.

Maguire *et al.*, (2001) and Renneson *et al.*, (2009) multiplied their α values (short-term) by 2.75 (long-term) and Paulter and Sims (2000) by 1.8 to allow for slow P sorption. For example, for 84 Dutch topsoils, van der Zee and van Riemsdijk (1988) reported an α value of 0.48 (s.d. = 0.09) after 40 h of sorption, but an α value of 0.61 (s.d. = 0.13) after 249 days of sorption, and consequently suggested multiplying short-term estimates of α by 1.8 to adjust for slow P sorption kinetics. Irrespective of whether presented as short-term or calculated as long-term, the wide range in α values suggests there is a need to test the DPSS model based on α values calculated for soils with a wide range of P sorption capacities (PSC) and initial P concentrations (P_{init}).

Alternatively, the use of an α value may not be necessary. Since total P sorption capacity (PSC_t), calculated as the sum of P sorption capacity remaining (PSC_r) and P already sorbed as Ox-P (Equation 4.4), is the same as PSC_t calculated using α (Equation 4.2); a direct measure of PSC_t ought to be a more reliable way to estimate DPSS than using a generic α value.

Since OxAl and OxFe are not routinely undertaken in Australian analytical laboratories, and calculation of P sorption maxima (P_{max}) through measurement of a multi-point P sorption curve is time consuming and not suitable for commercial laboratories, a single-point P sorption method that may be used as a measure of PSC_r is required (Equation 4.5). Several references to relationships between P_{max} and single-point P sorption measures have been reported (Bache and Williams, 1971; Simard *et al.*, 1994). Thus, the single-point P sorption measure, phosphorus buffering index (PBI), which is routinely measured in Australia, could potentially be used. Probert and Moody (1998) demonstrated that the ratio of Colwell-P/single-point P sorption index was correlated with P intensity. Moody (2011) reported high correlation between Colwell-P/PBI_{+Colwell-P} and CaCl₂-P ($r^2=0.925$, $P<0.001$), for a range of soils sampled to 10 cm. Thus, it may be possible to calculate DPSS as shown in Equation 4.5 for the majority of Australian soils, at little or no additional cost, disregarding the need to calculate α , and measure OxAl, OxFe, and Ox-P. Calculation of DPSS using Australian measures should be undertaken for Australian soils which represent a range in PSC's and P_{init} concentrations. These should be compared to CaCl₂-P concentrations to establish DPSS thresholds above which environmental P loss is considered unacceptable; and to Olsen-P and Colwell-P concentrations, to discern the P supplying potential of soils for optimum agronomic production.

$$DPSS = [Ox-P / \alpha(OxAl+OxFe)] \times 100 \quad (4.1)$$

$$PSC_t = \alpha(OxAl+OxFe) \quad (4.2)$$

$$\alpha = PSC_r + Ox-P / OxAl+OxFe \quad (4.3)$$

$$PSC_t = PSC_r + Ox-P \quad (4.4)$$

$$DPSS = [Ox-P / (PSC_r + Ox-P)] \times 100 \quad (4.5)$$

Schoumans and Groenendijk (2000) identified a critical DPSS threshold of 25%, above which the dissolved P concentration in the soil was observed to increase nonlinearly, increasing the risk of P loss for acid sandy soils from the Netherlands. This threshold was defined on the basis of a water quality standard of 0.1 mg P/L⁻¹ (Breeuwsma and Silva, 1992). Dougherty (2006) reported that for relatively high Bray-P and DPSS values, the concentrations of P in runoff from Australian soils appeared to be substantially higher than those of the northern hemisphere. This suggests that at least some Australian soils are at greater risk of P loss than are many soils elsewhere, suggesting their DPSS thresholds would be lower. Thus, comparison of DPSS to soil CaCl₂-P concentrations is warranted for a range of soils and P_{init} concentrations.

This study reports the P intensity and quantity pools, and P sorption values, for six field pasture soils of varying P sorption properties, each with three distinct P_{init} concentrations established by prior P fertiliser application. Depending on P_{init} treatment, the soils were sampled 6 and either 36 or 48 months after the final P fertiliser application. The objectives were to: 1) determine the change in P intensity and quantity extraction concentrations in soils from which on-going fertiliser P had been withheld, 2) assess the influence of soil PSC and P_{init} concentration on these intensity and quantity changes, 3) calculate and compare α values for soils with a range of PSCs and P_{init} concentrations, 4) assess different methods of calculating DPSS, without the need of an α value, and 5) identify relationships between the various quantity and intensity extractions and DPSS, to estimate the P supplying potential of, and risk of P loss from, a soil.

MATERIALS AND METHODS

Experimental management, treatments and characterisation

The field soils (0-10 cm) used in the current study were those reported on in Chapter 2. Briefly, the six replicated field soils in north-west Tasmania, Australia, encompassed a wide range of properties typical of soils supporting intensive dairy pasture production in Australia (Table 2.1). Soils were characterised by sampling the surface 10 cm randomly across the trial sites before fertiliser treatment application (Table 2.1). Triple superphosphate was applied at study establishment according to each soil's PSC, measured using the PBI, to create four P_{init} categories (referred to as 1, 2, 3 and 4) spanning from below to well above agronomic optimum for each soil. In this study, only soil from the two lowest and the highest P_{init} categories (1, 2 and 4), sampled in late 2005/2006 (6 months after the final fertiliser treatment) and late 2009, were selected for further analysis. The initial sample date was 12 months later for P_{init} Category 4 than the other categories due to reapplication of P fertiliser to achieve the target P_{init} concentration (detailed further in Chapter 2).

Chemical Analyses

Chapter 2 – chemical analyses and Table 2.1 – details the characteristics of the soils studied. Soil samples were analysed for 0.01 M CaCl₂- (Houba *et al.*, 2000), Olsen- (Olsen *et al.*, 1954) and Colwell- (Colwell, 1963) extractable P, and unadjusted PBI (Burkitt *et al.*, 2008) as part of the original study (Chapter 2). Briefly, PBI was measured by shaking 1 g of soil for 17 h in 0.01 M CaCl₂ with an addition of 1000 mg P/kg soil. The difference between the added P and the final P concentration in the equilibrating solution was the amount of P sorbed, with PBI calculated as P sorbed (mg/kg) / [final P solution (mg/L)^{0.41}] (Burkitt *et al.*, 2008). Additional measures for the current study included acid ammonium oxalate extracts for amorphous forms of P (Ox-P), Al (OxAl) and Fe (OxFe) (Tamm, 1922), total-P (Pt) determined by the Kjeldahl method of Allen and Jeffery (1990), total Pi (Saunders and Williams, 1955), and Po by difference between Kjeldahl Pt and H₂SO₄ soluble Pi. Phosphorus concentrations in all extracts were determined colorimetrically using the method of Murphy and Riley (1962), except in the oxalate extracts where P was determined by inductively coupled plasma atomic emission spectrophotometry (ICP-AES).

In addition, three measures of P sorption capacity remaining (PSCr) were made by 1) fitting a linear version of the Langmuir equation to P sorbed after addition of 0, 200, 400, 600, 800, 1000, 1250 and 1500 mg P/kg from each of the six soils (Olsen and Watanabe, 1957) and calculating the P sorbed maxima (PSC_{Pmax}); 2) determining the amount of P sorbed from a single addition of 1500 mg P/kg (PSCr₁₅₀₀) as part of the P_{max} measurement, and 3) determining the amount of P sorbed from a single P addition of 1000 mg/kg (PSCr₁₀₀₀), as per the PBI method (Burkitt *et al.*, 2008). All extractions were for 17 hours. Since P_{max} and PSCr₁₅₀₀ were calculated using the soils sampled to characterise the trial sites before P fertiliser treatment, mean initial Ox-P or Colwell-P from P Category 1 (control) only was added to PSCr₁₅₀₀ to calculate total P sorption capacity (PSCt) (Table 4.1). Since Ox-P, Colwell-P (Col-P) and PSCr₁₀₀₀ were measured for each treatment, the respective Ox-P and Colwell-P concentrations were added to PSCr₁₀₀₀ (PSCt_{1000+Ox-P} and PSCt_{1000+Col-P}) to calculate PSCt (Table 4.1). No addition of previously sorbed P (Ox-P or Colwell-P) was required for PSC_{Pmax} (Table 4.1). In addition to $\alpha_{0.5}$ which is used in the Netherlands, plot-specific α values were calculated to define the DPSS for each P sorption measure (Table 4.1). Alpha values were calculated by dividing each PSCt by the sum of OxAl and OxFe (Equation 4.3). Degree of P sorption saturation was calculated according to Equations 4.1 and 4.5 (Table 4.1). Change in DPSS_{Ox-P: α_{Pmax} (calculated as shown in Table 4.1) was compared over the course of the study.}

Statistical Analyses

Analysis of variance (ANOVA) was undertaken to assess the influence of P_{init} category and soil on initial and final values of all measures, and their change over time. Where the ANOVA showed significant treatment differences, means were separated at a significance level of 5% using Fisher's protected least significant difference (LSD). Simple and multiple linear regression analyses were used to identify key parameters associated with variation in the soil P measures. All statistical analyses were performed using GenStat 13th Edition (VSN International, 2010).

Table 4.1. The various P sorption measures, and their combinations, used to calculate alpha (α) and the degree of phosphorus sorption saturation (DPSS)

<i>Alpha value identification</i>	<i>Alpha calculation (Equation 4.3)</i>
$\alpha_{0.5}$	0.5
α_{pmax}	$PSCt_{pmax} / (OxAl + OxFe)$
$\alpha_{1000+Ox-P}$	$PSCr_{1000+Ox-P} / (OxAl + OxFe)$
$\alpha_{1000+Col-P}$	$PSCr_{1000+Col-P} / (OxAl + OxFe)$
$\alpha_{1500+Ox-P}$	$PSCr_{1500+Ox-P} / (OxAl + OxFe)$
$\alpha_{1500+Col-P}$	$PSCr_{1500+Col-P} / (OxAl + OxFe)$
<i>DPSS identification</i>	<i>DPSS calculation (Equation 4.1)</i>
$DPSS_{Ox-P:\alpha_{0.5}}$	$Ox-P / \alpha_{0.5} (OxAl + OxFe) \times 100$
$DPSS_{Ox-P:\alpha_{pmax}}$	$Ox-P / \alpha_{pmax} (OxAl + OxFe) \times 100$
$DPSS_{Ox-P:\alpha_{1000+Ox-P}}$	$Ox-P / \alpha_{1000+Ox-P} (OxAl + OxFe) \times 100$
$DPSS_{Ox-P:\alpha_{1000+Col-P}}$	$Ox-P / \alpha_{1000+Col-P} (OxAl + OxFe) \times 100$
$DPSS_{Ox-P:\alpha_{1500+Ox-P}}$	$Ox-P / \alpha_{1500+Ox-P} (OxAl + OxFe) \times 100$
$DPSS_{Ox-P:\alpha_{1500+Col-P}}$	$Ox-P / \alpha_{1500+Col-P} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{0.5}}$	$Col-P / \alpha_{0.5} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{pmax}}$	$Col-P / \alpha_{pmax} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{1000+Ox-P}}$	$Col-P / \alpha_{1000+Ox-P} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{1000+Col-P}}$	$Col-P / \alpha_{1000+Col-P} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{1500+Col-P}}$	$Col-P / \alpha_{1500+Col-P} (OxAl + OxFe) \times 100$
$DPSS_{Col-P:\alpha_{1500+Ox-P}}$	$Col-P / \alpha_{1500+Ox-P} (OxAl + OxFe) \times 100$
<i>DPSS identification</i>	<i>DPSS calculation (Equation 4.5)</i>
$DPSS_{Ox-P:PSCt_{1000+Ox-P}}$	$(Ox-P / Ox-P + PSCr_{1000}) \times 100$
$DPSS_{Ox-P:PSCt_{1500+Ox-P}}$	$(Ox-P / Ox-P + PSCr_{1500}) \times 100$
$DPSS_{Ox-P:PSCt_{pmax}}$	$(Ox-P / PSCt_{pmax}) \times 100$
$DPSS_{Col-P:PSCt_{1000+Col-P}}$	$(Col-P / Col-P + PSCr_{1000}) \times 100$
$DPSS_{Col-P:PSCt_{1500+Col-P}}$	$(Col-P / Col-P + PSCr_{1500}) \times 100$
$DPSS_{Col-P:PSCt_{pmax}}$	$(Col-P / PSCt_{pmax}) \times 100$

RESULTS AND DISCUSSION

Influence of soil and P_{init} category on initial and final extractable P concentrations, OxAl, OxFe, PBI and $DPSS_{Ox-P:\alpha_{Pmax}}$

The establishment P fertiliser treatment created a broad range of P_{init} concentrations (Table 4.2) across the majority of the soils studied. As a result, there were significant ($P < 0.05$) effects of soil and P_{init} category, and a significant interaction, on P measured by the majority of the extracts. However, PBI was not influenced by P_{init} category (Table 4.2), suggesting there was not enough sorption to influence PBI 6 or 36 to 48 months after fertiliser treatment. Our inability to create distinct P_{init} categories for Soil 3 may have limited the overall effect of P_{init} category on PBI.

Even after application of up to 500 kg P/ha, mean Pt, Olsen-P, Colwell-P, Ox-P concentrations, and $DPSS_{Ox-P:\alpha_{Pmax}}$ of Soil 3 were similar to those measured for the control treatment. Thus, they were significantly ($P < 0.05$) lower than all other soils (Table 4.2). In contrast, initial $CaCl_2$ -P concentrations for Soils 3 and 6 were approximately 5-22 fold greater ($P < 0.05$) than those of any other soil, were higher the greater the P_{init} category, and Soil 3 had significantly higher $CaCl_2$ -P concentrations ($P < 0.05$) than Soil 6 (Table 4.2). Soils 3 and 6, a Podsol and Hydrosol, respectively, had extremely low and very low PBIs due to their high sand and low clay, silt, OxAl, and OxFe contents. The other soils studied were a Kurosol (Soil 2), Dermosol (Soil 5) and a Ferrosol (Soil 1), all with greater PBIs than Soils 3, 4 and 6. Soil 4, also a Dermosol, had a similar PBI and OxAl content as Soil 6, but a higher OxFe and lower sand content. Across all soils, initial $CaCl_2$ -P concentrations ranged from 0.4 to 22.4 mg/kg.

The high P intensity in Soil 3 suggests that the majority of the sorption sites of this extremely low PBI soil may have been saturated, with the majority of P readily available in soil solution. However, the initial $DPSS_{Ox-P:\alpha_{Pmax}}$ of Soil 3 was only 14%, while initial $DPSS_{Ox-P:\alpha_{Pmax}}$ of the other soils ranged from 31 (Soil 6) to 45% (Soil 4) (Table 4.2). $DPSS_{Ox-P:\alpha_{Pmax}}$ of Soil 3 decreased to 7%, 30 or 42 months later, consistent with the observed increase in PBI of Soil 3 (Table 4.2), presumably due to desorption of P. Soil 3's inability to retain the treatment fertiliser P at site establishment may have been due to the presence of few P sorbing hydrous oxides of Fe and Al, its coarse texture (Leclerc *et al.*, 2001) and high organic carbon content blocking further P sorption (Lewis *et al.*, 1981), allowing movement of P from the sampling zone. Similarly, Nair and Harris (2004) reported that further addition of P to soils which had low Mehlich 1-P concentrations ($< 15 \text{ mg P kg}^{-1}$), and little P sorbing capacity, could result in a risk of environmental loss. Other similarly low $DPSS$ soils in the literature may have been missed if the generic $\alpha_{0.5}$ was used since $DPSS_{Ox-P:\alpha_{0.5}}$ for Soil 3 was 35%, decreasing to 20%.

Table 4.2. Mean initial value for each measure across all P_{init} categories, and across all soils, and their % change (% Δ) after 30 (P_{init} Category 4) or 42 months (P_{init} Categories 1 and 2)

Letters denote significant ($P < 0.05$) differences between soils across all P_{init} categories, and between P_{init} categories across all soils, respectively.

All units are mg/kg except PBI which has no units and DPSS which is a % and is presented as an absolute change rather than % change.

	Initial Pt	% Δ Pt	Initial Pi	% Δ Pi	Initial Po	% Δ Po	Initial CaCl ₂ -P	% Δ CaCl ₂ -P	Initial Olsen-P	% Δ Olsen-P	Initial Colwell-P	% Δ Colwell-P	Initial Ox-P	% Δ Ox-P	Initial PBI	% Δ PBI	Initial DPSS OxP: α_{Pmax}	Δ DPSS OxP: α_{Pmax}
<i>Soil</i>	<i>All P_{init} categories</i>																	
1	1279e	-7b	562d	-24a	717d	18b	0.42a	-8c	40.8c	-29b	187d	-14bc	687d	-17bc	628e	4a	37cd	-7ab
2	602d	-1bc	305c	-7a	297b	3ab	0.70a	-45b	39.4c	-28b	137c	-12bcd	377c	-11cd	244c	-3a	33bc	-3bc
3	245a	-21a	54a	-11a	191a	-20a	22.36c	-71a	15.7a	-58a	20a	-27ab	75a	-46a	25a	161b	14a	-7ab
4	480c	8c	237c	-1a	243ab	23b	2.61a	-43b	38.3bc	-16c	131c	-9cd	350c	-12c	102b	27a	45e	-6ab
5	1345f	23d	724e	-2a	621c	94c	0.37a	-29bc	29.6b	-9c	149c	5d	867e	-1d	525d	-13a	41de	-<1c
6	431b	-5b	139b	-41a	292b	14b	13.25b	-49ab	38.8bc	-38b	89b	-34a	234b	-25b	42ab	13a	31b	-10a
<i>P_{init}</i>	<i>All soils</i>																	
1	627a	5b	201a	-7a	426b	12a	4.16a	-22b	16.3a	-16b	49a	3b	278a	-9b	274a	41a	22a	-1c
2	676b	-5a	236a	-18a	440b	3a	5.31a	-32b	18.6a	-35a	59a	-22a	327b	-24a	266a	-6a	25a	-5b
4	889c	-1ab	574b	-18a	315a	26b	10.38b	-70a	66.4b	-39a	249b	-28a	690c	-23a	244a	59a	53b	-10a

Influence of soil on calculation of alpha (α) and PSCt

In the current paper, α is an empirical parameter which has been used to relate PSCt to the sum of OxAl and OxFe, or other P sorption capacity measures, to allow comparison between different estimated DPSS values. For soils from Belgium (Renneson *et al.*, 2009) and America (Paulter and Sims, 2000), the use of a generic α value of 0.5 across a range of soils was suggested as not being ideal. In the current study, analysis of variance revealed that for each α calculation method, there was significant ($P < 0.05$) variation in α values between soils, with α values of the lower PBI soils being greater ($P < 0.05$) than those for the higher PBI soils (Table 4.3). The high α values for Soil 3 were due to its extremely low Ox-P, OxFe and OxAl contents rather than its P_{\max} since very low PBI Soils 4 and 6 had similar P_{\max} values but greater Ox-P, OxFe and OxAl contents.

In contrast, the inclusion of high PBI soils in the current study led to α values of these soils being lower than reported in the literature for European and American soils. For example, the mean short-term α value reported by Paulter and Sims (2000) was 0.38 for a range of surface soils (0-20 cm). Using Renneson *et al.*'s., (2009) mean Ox-P, OxAl and OxFe concentrations, and long-term α values (mean of 0.66; ranging from 0.43 to 0.93), we calculated that Renneson *et al.*'s., (2009) mean short-term α value was 0.37 (ranging from 0.28 to 0.47). Some of our soils had a larger content of amorphous hydrous oxides of Al and Fe (mean 886 mmol/kg), which are the most active P binding sites (Paulter and Sims, 2000; Burkitt *et al.*, 2002b; Burkitt *et al.*, 2006), than reported for Irish (217 mmol/kg) (Maguire *et al.*, 2001), Belgian (76 mmol/kg) (Renneson *et al.*, 2009), and American and Dutch (41 to 61 mmol/kg) (Paulter and Sims, 2000) soils. Differences in geomorphology and age (Birkeland, 1984) between international soils could contribute to the various OxAl and OxFe contents. Since α relates PSCt to the sum of OxAl and OxFe, our smaller ratio of PSCt to the sum of OxAl and OxFe resulted in our smaller α values for high PBI soils.

The contrasting α values between extremely low and high PBI soils brings into question whether the inclusion of an α value, which is likely to be soil specific, is required when a direct measure of a soil's PSCr, and calculation of PSCt, could be used instead i.e. Equation 4.5. This is especially the case since OxAl, OxFe and Ox-P, which are used to calculate α , are not routinely measured in Australian analytical laboratories, while PBI and Colwell-P extractions, which could be used to calculate PSCt, are. Indeed, the DPSS was the same irrespective of whether Equation 4.1, using soil specific α values, or Equation 4.5, was used i.e. $DPSS_{Ox-P:\alpha_{Pmax}} = DPSS_{Ox-P:PSCt_{Pmax}}$.

Long-term α (α_{lt}) values calculated with either Ox-P or Colwell-P were not different ($P > 0.05$) from each other, but were greater than all our other α values (Table 4.3). When calculated across all soils, our α_{lt} values (0.87 for Ox-P and 0.78 for Colwell-P) were greater than those reported elsewhere in the literature. Mean α_{lt} reported by Renneson *et al.*, (2009) for the surface 20 cm of Belgian sandy soils was 0.66, and for the surface 7.5 cm of Irish soils, Maguire *et al.*, (2001) reported a mean α_{lt} value of 0.65. In calculating long-term α values, we and Renneson *et al.*, (2009) multiplied PSCr by 2.75, as suggested by Maguire *et al.*, (2001). If Paulter and Sims (2000) multiplied their short-term α value of 0.38 by 2.75 (instead of 1.8), their α value would have been 1.0, which is greater than our mean value across all soils. However, just like the short-term α values,

for our extremely low PBI Soil 3 and very low PBI Soil 6, our α_{it} values were greater than those of Paulter and Sims (2000). Thus, not only is the use of a generic α value questionable, but so too is the use of an α value to scale PSCT and OxAl and OxFe for a range of P sorption capacity soils.

Table 4.3. Comparison of α values calculated using single- and multi-point sorption measures, Colwell-P (Col-P), and Ox-P

Soil	$\alpha_{1000Ox-P}$	$\alpha_{1000Col-P}$	$\alpha_{1500Ox-P}$	$\alpha_{1500Col-P}$	α_{ltOx-P}	$\alpha_{ltCol-P}$	α_{Pmax}
1	0.08a	0.10a	0.17a	0.13ab	0.38a	0.34ab	0.15a
2	0.14b	0.17b	0.24a	0.19b	0.53a	0.48b	0.21a
3	0.43e	0.48e	0.63c	0.50d	1.43c	1.30d	1.25d
4	0.22c	0.28c	0.40b	0.29c	0.80b	0.70c	0.37b
5	0.07a	0.09a	0.16a	0.10a	0.32a	0.27a	0.16a
6	0.28d	0.38d	0.81d	0.65e	1.77d	1.61e	0.88c
<i>Mean</i>							
All	0.21a	0.25a	0.40ab	0.31ab	0.87c	0.78c	0.50b

Letters within columns for each α value calculation method signify significant ($P<0.05$) differences between soil means.

Letters within the mean row signify significant ($P<0.05$) differences between the different methods of calculating α .

Influence of soil and calculation method on DPSS

The majority of the DPSS percentages calculated using the equations listed in Table 4.1 were significantly ($P<0.05$) different from each other when statistically analysed across all soils and P_{init} concentrations (Table 4.5). The exceptions were; $DPSS_{Col-P:\alpha_{1000Ox-P}}$ which was not significantly different from $DPSS_{Ox-P:\alpha_{0.5}}$; $DPSS_{Ox-P:\alpha_{1500Ox-P}}$ which was not different from $DPSS_{Ox-P:\alpha_{Pmax}}$; and $DPSS_{Col-P:\alpha_{Pmax}}$ and $DPSS_{Col-P:\alpha_{0.5}}$ which were not different from each other (Table 4.4). The variability in DPSS according to its calculation method means that when alternative methods of calculating DPSS are developed, new thresholds may be required.

Soil differences may also give rise to different DPSS thresholds. McDowell *et al.*, (2001a) reported that soils from New Zealand, the UK and USA had $DPSS_{Ox-P:\alpha_{0.5}}$ thresholds of 25-34%, above which $CaCl_2$ -P concentrations increased rapidly. Our study revealed that the DPSS after which $CaCl_2$ -P concentrations were above the environmental threshold of 0.5 mg/kg (0.1 mg/L) varied according to soil (Figure 4.1). For example, soil $CaCl_2$ -P concentrations were above 0.5 mg/kg when $DPSS_{Ox-P:\alpha_{Pmax}}$ of Soils 1 and 5 were ~60%, Soil 2 ~45%, Soil 3 <5%, Soil 4 <20%, and Soil 6 ~10%, (Figure 4.1). This means that a universal DPSS threshold of 25% is inappropriate and highlights the need to identify the most suitable method of relating quantity and intensity factors across a range of soils, and correlating this with P loss, so that more robust soil specific thresholds can be identified. In addition, water quality standards would influence threshold DPSS since they are likely to vary from the threshold we used as an indicator.

Table 4.4. Degree of P sorption saturation (DPSS) percentages which were not significantly ($P>0.05$) different from at least one measure of DPSS, calculated using single- and multi-point sorption measures, and Colwell-P (Col-P) and Ox-P

All other DPSS calculated as detailed in Table 4.1 were significantly ($P<0.05$) different from each other

	DPSS _{Ox-P:} $\alpha_{1500+Ox-P}$	DPSS _{Col-P:} α_{Pmax}	DPSS _{Col-P:} $\alpha_{1000+Ox-P}$	DPSS _{Ox-P:} $\alpha_{0.5}$	DPSS _{Ox-P:} α_{Pmax}	DPSS _{Col-P:} $\alpha_{0.5}$
<i>Soil</i>	<i>Across all P_{init} categories</i>					
1	29a	10b	19a	11a	37bc	3a
2	28a	12bc	17a	14a	33b	5a
3	28a	4a	11a	35b	14a	9ab
4	40b	17c	41b	33b	45d	12b
5	42b	7ab	15a	13a	41cd	2a
6	32a	12b	47b	52c	31b	20c
<i>P_{init}</i>	<i>Across all soils</i>					
1	27a	5a	12a	18a	22a	5a
2	28a	5a	10a	21a	25a	5a
4	44b	21b	53b	40b	53b	15b
All	33c	<i>Across all P_{init} categories and soils</i>				9a
		10a	25b	26b	34c	

Letters within the same column section i.e. across all P_{init} categories, and row when analysed across all soils and P_{init} categories, signify significant ($P<0.05$) differences between means in that column or row.

Absolute change and % change in soil extractable P, OxAl, OxFe, PBI and DPSS_{Ox-P:} α_{Pmax} and % change of Pt

Withholding fertiliser for 30 or 42 months resulted in a decrease ($P<0.05$) in the majority of the P quantity and intensity measures (Table 4.2). This suggests; 1) labile P moved into non-labile pools that were not Olsen, Colwell or Oxalate extractable, i.e. immobilised as Po or precipitated, or/and 2) P was exported and/or lost to the surrounding environment. However, no significant ($P<0.05$) change in Pt (absolute or relative) was measured (Table 4.2), suggesting that either Pt was not sensitive enough to reflect P exports and losses, or that the exports and losses were relatively small.

We suggest that the majority of the decrease in Pi was due to conversion to Po in plant, animal and microbial residues. Based on pasture production and pasture P concentrations reported by Burkitt *et al.*, (2010a) and Cotching and Burkitt (2011), between 14 (Soil 2) and 56 (Soil 6) kg P/ha.yr was estimated to be taken up by pastures for these field soils. Assuming 80% of the consumed P was returned in dung (Haynes and Williams, 1993), of which 36% was labile Po (Aarons *et al.*, 2004), Po concentrations were expected to increase by 5 mg/kg (Soil 2) to 20 mg/kg (Soil 6) (5 and 26 kg/ha, respectively), which was approximately half of the increases observed for some of the soils. Across the majority of the soils, conversion of Pi to Po appeared to be a greater contributor than P sorption to the decrease in extractable P, since PBI did not significantly change

($P > 0.05$) when analysed across all soils and P_{init} categories, and all quantity measures (Olsen-P, Colwell-P, Ox-P and $DPSS_{Ox-P:\alpha P_{max}}$) decreased (Table 4.2). This suggests that not only was labile Pi converted to Po, but some previously sorbed P may also have been converted. Some previously sorbed P could also have been exported in animal product or through environmental loss.

The Po concentrations (46-77% of Pt) of the current study were greater than the 5 to 30% reported by Perrott *et al.*, (1992) and Oberson *et al.*, (2001), but similar to the 45 to 57% reported by Condon and Goh (1989) for grassland soils after Pi fertiliser application. Initial and final Po concentrations did not reflect increasing P_{init} category, but were similar across all P_{init} categories. This suggests that turnover in plant and animal excreta contributed to these Po increases, rather than a flush in microbial population and activity immobilising applied P fertiliser into Po. This finding is supported by Doolette *et al.*, (2011) who, using solution ^{31}P nuclear magnetic resonance spectroscopy on a selection of the soils used in the current study (Soils 1, 2, 5 and 6), found that the majority of the differences in Pt between P_{init} Categories 1 and 4 were due to an increase in Pi, except for Soil 6 which was due to an increase in Po. Interestingly, after application of 34 and 51 kg P/ha, Condon and Goh (1989) reported that the rate of Po accumulation declined after several years (1958-1971), and suggested Po was reaching a steady state. After reviewing studies conducted on the Winchmore trial site in New Zealand, McDowell and Condon (2012) concluded that beyond a certain Pt concentration, additional P did not accumulate as Po, but as Pi. This suggests that the majority of the current study's soils had reached a steady state of Po accumulation, and that, therefore, there was no influence of P_{init} category on final Po.

The greater Po content for P_{init} Category 4 when compared to the control, which was reported by Doolette *et al.*, (2011) for Soil 6, was not observed when Po was calculated as the difference between Pt and Pi for the current study. Doolette *et al.*, (2011) provided no explanation as to why Soil 6 behaved differently to Soils 1, 2 and 5. However, in support of Doolette *et al.*'s, (2011) findings for Soil 6, Murphy and Sims (2012) reported that P applied as orthophosphate was rapidly (within 18 h) converted to molybdate-unreactive forms i.e. highly soluble Po, by micro-organisms. If Doolette *et al.* (2011) had assessed Soil 3, similar increases in Po may have been observed due to it having similar soil characteristics as Soil 6. However, as already mentioned, Pt did not increase for Soil 3 after P fertiliser application. Total-P decreased over the monitoring period of the current study for Soil 3, leading to an overall decrease in Po of -40 mg/kg (20%) (Table 4.2). This decrease in Po would most likely have been due to microbial mineralisation (Chapter 5). Soils 3's coarse-texture, good drainage, and high OM content, would provide favourable conditions for microbial uptake of P and mineralisation of Po. In addition, since Soil 3 is a Podzol, with an extremely low PBI, and low pH, Pi released from the fertiliser and microbes would be liable to leaching (Chapter 6). Soil 3 also desorbed the most P, evident by it having the greatest ($P < 0.05$) absolute and relative increase in PBI (Table 4.2), and the greatest relative decrease in $DPSS_{OxP:\alpha P_{max}}$. When expressed as a % of Pt, initial and final Pi and Po concentrations of Soil 3 remained at 23 and 77%, respectively, due to the 21% decrease in Pt (Table 4.2). The potential movement of P from Soils 3 and 6 was also reflected in them showing the greatest relative decrease in both intensity ($CaCl_2$ -P) and quantity (Olsen-P, Colwell-P and Ox-P) measures (Table 4.2).

The generally small decrease in Pt for the majority of the soils was thought to be due to the small estimates of P exports (5 to 13 kg P/ha.yr) over the study period and the relatively low sensitivity of the Pt method. In contrast to all other soils where Pt decreased, Pt of Soil 5 increased by 23% or 317 mg/kg. In addition, the Po of Soil 5 increased 6 to 78 times more than the other soils ($P<0.05$) (Table 4.2). When Soil 5 was excluded from the statistical analysis, there was no effect of P_{init} category or soil interaction for final Po, whereas there was a soil by P_{init} category interaction ($P<0.05$) for final Po when analysed across all soils and P_{init} concentrations. The large increase in Po of Soil 5 also contrasted with the relatively small decreases in Pi, Ox-P and $DPSS_{Ox-P:\alpha_{Pmax}}$. Since Po was calculated as the difference between Pi and Pt, the apparent large increase in Po of Soil 5 may have resulted from the underestimation of the initial Pt of Category 4. Mean initial Pt of Category 4 was 1366 mg/kg, which was similar to the initial Pt means of Categories 1 and 2 (1313 and 1352 mg/kg), while final Pt for Category 4 was 1845 mg/kg (25% increase). This is supported by Doolette *et al.* (2011) who reported a difference of approximately 400 mg/kg between Categories 1 and 4 of Soil 5 when sampled after fertiliser application, and when using the method of Saunders and Williams (1955). This suggests that the Pt increase, and resultant Po increase, of Soil 5 was not a real effect, thus, there was not a P_{init} category by soil interaction ($P<0.05$) for final Po.

Relationship between the different P extractions, OxAl, OxFE, PBI and $DPSS_{Ox-P:\alpha_{Pmax}}$

Paulter and Sims (2000) reported that curvilinear equations best described relationships between DPSS and $CaCl_2$ -P for the surface 20 cm of 41 soils ($r^2=0.65$ to $r^2=0.82$; $P<0.001$). When McDowell *et al.*, (2001a) applied split-line models to such data, thresholds or “change points” were identified at DPSS of 25-34%. However, two of their soils did not display a change point, which they attributed to them not being sufficiently saturated with P. When we plotted $CaCl_2$ -P against $DPSS_{Ox-P:\alpha_{Pmax}}$ for Soil 3, a linear relationship resulted in a slightly better fit compared to a curvilinear relationship ($r^2=0.79$ versus $r^2=0.77$) (Figure 4.1). Koopmans *et al.*, (2002) suggested that linear relationships between DPSS and water extractable P (WEP) may reflect a narrow range in soil P concentrations, too narrow to show a nonlinear relationship. This is true of Soil 3, since, although there was a wide range in $CaCl_2$ -P concentrations, the range in $DPSS_{Ox-P:\alpha_{Pmax}}$ was small.

The sum of soil OxAl and OxFE was initially developed as a good predictor of PSC for acidic sandy soils (Schoumans and Groenendijk, 2000). In addition to amorphous hydrous oxides of Al and Fe, other sites for P sorption include clay (Burkitt *et al.*, 2002b), organically complexed metals, and diffusion into particles of microcrystalline Al and Fe oxides (Barrow, 1983b). Thus, the relationship between PSC and OxAl and OxFE could be expected to weaken if other modes of P sorption have a greater influence on a soil's PSC. However, the various single- and multi-point PSCr measures used to calculate DPSS in the current study were highly correlated with the sum of OxFE and OxAl for the range of soils studied (Figure 4.2). This suggests that the PSC's of the soil's are largely controlled by the hydrous oxides of Al and Fe (Paulter and Sims, 2000; Burkitt *et al.*, 2002b; Burkitt *et al.*, 2006). This further supports the calculation of DPSS using Equation 4.5, and measurement of the soils PSCr and P already sorbed, rather than Equation 4.1, which requires measurement of OxAl and OxFE, and calculation of an α value.

Both Ox-P and Colwell-P are quantity measures which could be used to represent the already sorbed P. Indeed, Ox-P and Colwell-P were well correlated for the majority of the soils (r^2 ranged from 0.57 for Soil 3 through to 0.99 for Soil 1). Multiple linear regressions revealed a significant relationship between Ox-P, Colwell-P and PBI [Initial Ox-P = $-162.1 + (2.130 \times \text{initial Colwell P}) + (0.4923 \times \text{initial PBI})$ ($P < 0.001$; $r^2 = 0.84$)]. Thus, the conversion factor between Ox-P and Colwell-P changed according to PBI. This explains why DPSS values depended on whether they were calculated using Ox-P or Colwell-P, and suggests Colwell-P cannot simply substitute for Ox-P unless the resultant DPSS using Colwell-P is correlated with the risk of environmental loss. There was also a relationship between Ox-P and other sorption measures i.e. initial Ox-P = $-3.8 + (2.1207 \times \text{initial Colwell-P}) + (0.04395 \times \text{initial OxFe}) - (0.001124 \times \text{initial OxAI})$ ($P < 0.001$; $r^2 = 0.95$).

Rapid and simple P measures already routinely undertaken in Australian laboratories i.e. PSCr_{1000} as measured when calculating PBI, and Olsen-P or Colwell-P, could be used to calculate DPSS (Equation 4.5). The r^2 values for the relationships between $\text{CaCl}_2\text{-P}$ and $\text{DPSS}_{\text{Ox-P}:\alpha_{\text{Pmax}}}$ (Figure 4.1) were similar to those between $\text{CaCl}_2\text{-P}$ and $\text{DPSS}_{\text{Col-P}:\text{PSCt}_{1000+\text{Col-P}}}$ [r^2 ranged from 0.22 (Soil 6) to 0.88 (Soil 1) for the latter relationship]. Similarly, the r^2 values for $\text{DPSS}_{\text{Ols-P}:\text{PSCt}_{1000+\text{Ols-P}}}$ ranged from 0.29 (Soil 6) through to 0.88 (Soil 1). Probert and Moody (1998) demonstrated that the index of Colwell-P/single-point P sorption index was correlated with P intensity. Moody (2011) reported high correlation between Colwell-P/ $\text{PBI}_{\text{adjusted}}$ and $\text{CaCl}_2\text{-P}$ ($r^2 = 0.925$, $P < 0.001$), for a range of soils sampled to 10 cm. However, the r^2 values for Colwell-P/ $\text{PBI}_{\text{adjusted}}$ for the soils of this study ranged from 0.1 (Soil 6) through to 0.81 (Soil 4). When we used $\text{PBI}_{\text{unadjusted}}$ instead of PSCr_{1000} in Equation 4.5, the r^2 values were slightly larger; from 0.33 (Soils 5 and 6) to 0.85 (Soil 4). Soils with the capacity to sorb more than 1000 mg/kg are accounted for when calculating PBI by dividing the amount of P sorbed by the amount of P added, giving a proportion which is the same regardless of the amount of P added (Burkitt *et al.*, 2002b). Thus, it may be possible to calculate DPSS, as shown in Equation 4.5, using routine Australian extracts, i.e. Colwell-P and $\text{PBI}_{\text{unadjusted}}$, for the majority of Australian soils at little or no additional cost.

Ideally, a measure of soil P intensity (i.e. $\text{CaCl}_2\text{-P}$) should be combined with DPSS in order to significantly increase the proportion of P variation explained in the prediction of P loss to water or a soil's supply potential (Beauchemin and Simard, 1999). Soil $\text{CaCl}_2\text{-P}$ could provide an indication of the intensity of P in solution, while DPSS could indicate the soil's P capacity (Beauchemin and Simard, 1999). However, further work correlating DPSS calculated utilising Australian measures with P loss is essential in order to estimate the supplying potential of soil once P fertiliser has been withheld.

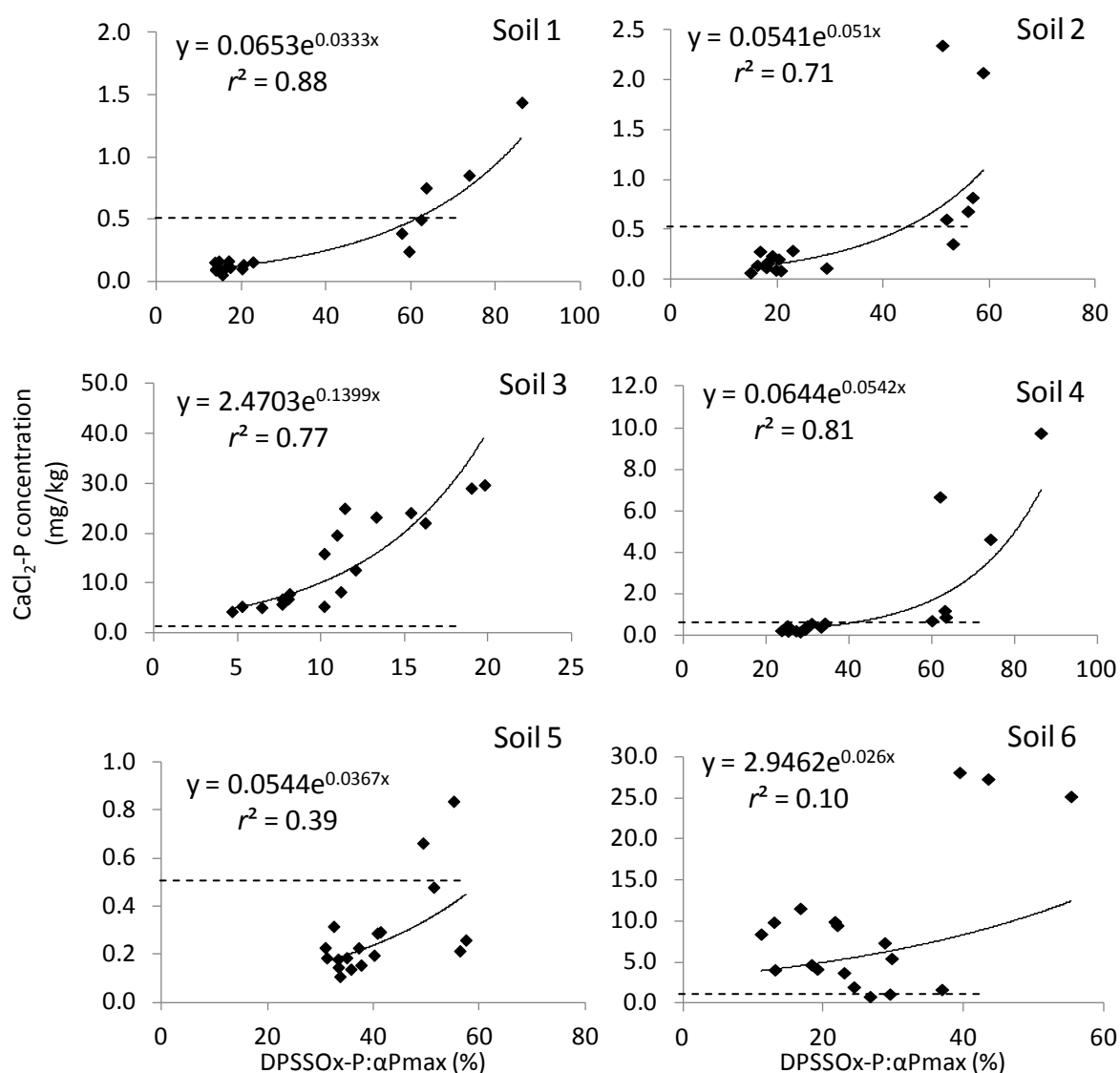


Figure 4.1. Relationship between $\text{CaCl}_2\text{-P}$ concentration and $\text{DPSSOx-P}:\alpha\text{Pmax}$ [calculated as $\text{Ox-P}/\alpha_{\text{Pmax}}(\text{OxAl}+\text{OxFe})\times 100$]. Note x- and y-axes are variable between soils. DPSS calculated using Equation 4.5 gave the same relationship with $\text{CaCl}_2\text{-P}$ as did DPSS calculated using Equation 4.1. Dashed lines indicate a nominal environmental threshold for $\text{CaCl}_2\text{-P}$ of 0.1 mg/L (0.5 mg/kg).

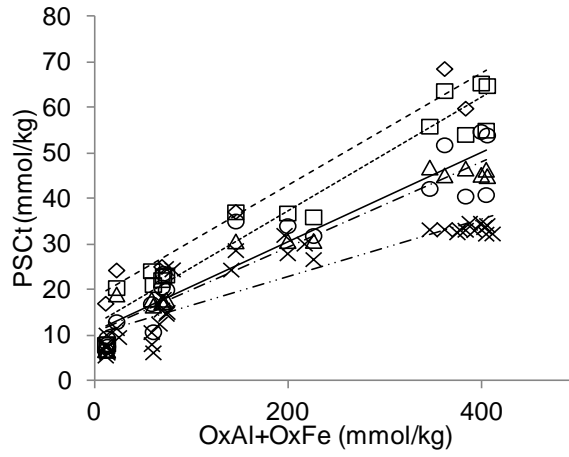


Figure 4.2. Relationship between the sum of OxAl and OxFe and single-point $\text{PSCT}_{1500+\text{Ox-P}}$ ($\cdots\Box\cdots$), $\text{PSCT}_{1500+\text{Col-P}}$ ($---\Delta---$), $\text{PSCT}_{1000+\text{Ox-P}}$ ($-O-$) and $\text{PSCT}_{1000+\text{Col-P}}$ ($---x---$) and multiple-point $\text{PSCT}_{\text{Pmax}}$ ($--\Diamond--$) measures.

$$\text{PSCT}_{\text{Pmax}} = 0.1233x + 18.252, r^2 = 0.96; \text{PSCT}_{1500+\text{Ox-P}} = 0.1246x + 12.253, r^2 = 0.95; \text{PSCT}_{1500\text{Col-P}} = 0.0945x + 10.158, r^2 = 0.95; \text{PSCT}_{1000+\text{Ox-P}} = 0.0981x + 10.748, r^2 = 0.90; \text{and } \text{PSCT}_{1000+\text{Col-P}} = 0.0636x + 10.221, r^2 = 0.83$$

CONCLUSION

The Australian soils of the current study contained $\text{CaCl}_2\text{-P}$ concentrations above 0.1 mg/L (0.5 mg/kg), even when $\text{DPSS}_{\text{Ox-P}:\alpha_{0.5}}$ was below 25%. This suggests DPSS thresholds would be lower for Australian soils than reported for other soils, internationally. However, when DPSS was calculated using soil specific α values or PSCr and compared to $\text{CaCl}_2\text{-P}$ concentrations, DPSS thresholds changed according to soil, being larger the greater the soil PSC. Thus, generic DPSS thresholds should not be used. This is particularly important for extremely low PBI soils which may have much lower DPSS thresholds than other soils.

This study supports calculation of DPSS using Olsen-P or Colwell-P as a measure of P already sorbed, and PBI or P sorbed from an addition of 1000 mg P/kg (as per PBI method), as a measure of PSCr. These measures are routinely undertaken in Australian laboratories, meaning DPSS could be calculated at no additional cost. This approach of calculating DPSS also means that calculation of soil-specific α values are not required. However, further correlation of DPSS with a measure of the risk of P loss, such as $\text{CaCl}_2\text{-P}$, is required across a larger range of Australian soils, and soil P concentrations, before critical DPSS thresholds can be identified for individual soil types.

Calculation of DPSS using Australian measures may also be used as a predictor of a soil's P supplying potential when used in combination with other soil P extractions. By withholding P fertiliser inputs, P intensity of heavily fertilised pasture soils decreased, reducing the risk of P loss. Quantity measures, such as Olsen-P, Colwell-P, PBI, and DPSS, of most of the soils studied also decreased, however, the majority of the P_i was thought to be converted to P_o rather than being exported or lost, as the case may be for Soil 3. Thus, there was enough P contained in the soil to supply plants in the absence of further P fertiliser applications for periods much greater than the 30 or 42 months monitored.

5

**CHANGES IN PHOSPHORUS FORMS AFTER THE REWETTING AND LONGER-TERM
INCUBATION OF SOILS WITH VARYING PHOSPHORUS STATUS AND BUFFERING
CAPACITIES**

ABSTRACT

Rapidly rewetting dry soil has been reported to increase extractable phosphorus (P) concentrations, and consequently, the potential for P loss to the environment – in the short-term at least. However, little is known of the longer term implications of rewetting dry soil. We examined the change in extractable soil P after drying and rewetting (DRW) by incubating six pasture soils spanning a wide range of P sorption capacities and initial P (P_{init}) concentrations. Increases in soil inorganic P (P_i) 418 days after DRW ranged from 47 to 211 mg/kg, respectively, for the soils with the lowest and highest P buffering indices (PBI). The majority of the increase in P_i was not reflected in increases in calcium chloride extractable-P ($\text{CaCl}_2\text{-P}$), Olsen-P or Colwell-P, nor in decreases in PBI. Although $\text{CaCl}_2\text{-P}$, Olsen-P and Colwell-P concentrations of the two soils with the lowest PBI, a Podosol and Hydrosol, significantly ($P < 0.001$) increased, these increases still only represented a small proportion of the released P_i . We hypothesise that the released P_i was either; partially immobilised within microbes, adsorbed to sesquioxide surfaces, absorbed into sesquioxide matrices through solid state diffusion, or precipitated. For field soils with very low and extremely low PBIs, loss of P released by DRW to the broader environment would be expected to occur soon after rewetting. Thus, microbial and physico-chemical changes due to DRW may further exacerbate the inherent P loss risk for very low and extremely low PBI soils.

INTRODUCTION

Phosphorus (P) losses via runoff and leaching from agricultural soils can impact on waterways (Carpenter *et al.*, 1998). Increases in inorganic soil P (P_i) status typically results in increases in runoff P concentrations (Sharpley and Rekolainen, 1997; Burkitt *et al.*, 2010b). Drying and rewetting (DRW) cycles have been found to increase P_i (Sparling, 1985; Turner *et al.*, 2002; Turner and Haygarth, 2003; Butterly and McNeill, 2011). This occurs through a number of biological and physico-chemical processes: 1) organic matter (OM) and microbial cells can be solubilised upon soil drying, 2) microbial cells can lyse upon rewetting, releasing principally organic P (P_o) (Turner and Haygarth, 2001), and 3) P_o can be hydrolysed (Magid and Nielsen, 1992; Turner and Haygarth, 2003; Butterly, 2008) by an increase in microbial activity. Further, microbial activity and physical disturbance of soil can lead to mineralisation of OM and P_o (Butterly and McNeill, 2011), solubilisation of precipitated P (Oberson and Joner, 2005), and desorption of weakly sorbed P (He and Zhu, 1997).

Under favourable conditions, microbial P can contribute substantial quantities of plant-available P (Grierson *et al.*, 1998) via mineralisation. Chen *et al.* (2003) calculated P release from the soil biomass to be 30 mg/kg.yr (14 kg/ha.yr) for a New Zealand grassland soil. Bünemann *et al.*, (2007) reported gross mineralisation rates of P_o of 0.9–1.2 mg/kg.day for three diverse pasture soils from southern Australia. However, microbes also immobilise P, with the concentration and forms of P varying widely according to cell age and P concentration of the soil (Oberson and Joner, 2005). Although variable, the microbial biomass of grassland soils has been reported to contain up to 7.5% of the total soil P (P_t), and range in concentration from 4 to >100 mg/kg (Oberson and Joner, 2005). Average P concentrations of 24.2 and 31.0 mg/g dry weight were reported for bacteria and fungi, respectively, grown in cultures of equal glucose and P content (Anderson and Domsch, 1980). After a single DRW cycle, microbial cell lysis has been reported to release between 40 and 66% of microbial P into extracting solutions (Brookes *et al.*, 1982; McLaughlin *et al.*, 1986; Wu and Brookes, 2005). Thus, large quantities of P can potentially be released due to DRW.

Turner and Haygarth (2001) suggested that more frequent cycles of DRW through irrigation and increasing climate variability may result in more microbial P being released into the surrounding environment. We hypothesise that sorption reactions, microbial immobilisation, and precipitation will, in most soils, result in the rapid removal of P that is released into the soil solution after DRW. However, soils with a low ability to sorb P may hold the released P in the soil solution until it is; taken up by plants and microbes, precipitated, and/or lost to the surrounding environment. However, further knowledge is required of the resultant magnitude and duration of changes in P pools in order to understand the P supplying potential of DRW to bio-available P pools and the surrounding environment. We investigated the changes in extractable-P after rewetting six soils which spanned a wide range of P sorption capacities, and each of which contained four distinct initial soil P concentrations (P_{init}).

MATERIALS AND METHODS

Experimental management, treatments and characterisation

The six soils used for the current study were from the field experiment described in Chapter 2. Thrice replicated stored samples of the four P_{init} concentration categories, which had not received on-going P_{fert} , were used for each soil. The soils were sampled six months after P fertiliser application, and were stored dry (oven dried at 40°C) at room temperature for a period of five years before being incubated.

Fourteen grams of dry soil was weighed into 40 ml polypropylene tubes. The soils were rewet with distilled water to 70% field capacity (FC) at room temperature and gently stirred with a spatula ensuring all soil remained in the tubes (Javid and Rowell, 2002; Butterly and McNeill, 2011). Soils were allowed to equilibrate for one day before the first batch of samples was destructively harvested and extracted. The remaining sample batches were placed in the incubator. Incubation was undertaken in a dark cabinet at 35°C. The moisture content of the samples was maintained at 70±10% FC by weighing at regular intervals and adding water as necessary. For each of the six soils and four P_{init} concentrations, there were five sample extraction times; after 1, 38, 114, 226, and 418 days. Soils were oven dried (40°C) and extracted directly after harvest. To assess if drying influenced calcium-chloride extractable-P ($CaCl_2$ -P) concentrations, a sub-sample was taken from each sample of the final batch (after 418 days of incubation), and $CaCl_2$ -P analysed without drying the soils directly beforehand i.e. they remained moist (70% FC). These un-dried samples were compared to samples from the same batch which were analysed for $CaCl_2$ -P after being oven dried.

Chemical Analyses

All samples were analysed for $CaCl_2$ -P as both a surrogate for P in the soil solution and an environmental risk indicator (McDowell and Sharpley, 2003; Moody, 2011). Calcium chloride-P was determined by using a modified version of the method of Houba *et al.*, (2000) involving shaking soil for 30 minutes with 0.01 M $CaCl_2$ using a soil:solution ratio of 1:5. Olsen-P (Olsen *et al.*, 1954), Colwell-P (Colwell, 1963), total Pi (Saunders and Williams, 1955), Po [calculated as the difference between total-P (Pt) and total Pi], and unadjusted P buffering index (PBI) (Burkitt *et al.*, 2008), were measured for the initial and final samples only. Olsen-P and Colwell-P are both common agronomic P measures in Australia, Colwell-P being a variant of the Olsen-P method with a longer shaking time (16 h) and wider soil:solution ratio (1:100). Total-P was determined by the Kjeldahl method (Allen and Jeffery, 1990) for the initial samples only, since there was no P removal during the incubation. Phosphorus buffering index was measured by shaking 1 g of soil for 17 h in 0.01 M $CaCl_2$ with an addition of 1000 mg P/kg soil. The difference between the added P and the final P concentration in the equilibrating solution was the amount of P sorbed, with PBI calculated as $P \text{ sorbed (mg/kg)} / [final P \text{ solution (mg/L)}^{0.41}]$ (Burkitt *et al.*, 2008). Inorganic solution P in all extracts was measured using the molybdenum blue method of Murphy and Riley (1962). All soils were extracted at room temperature.

Statistical Analysis

The effect of P_{init} categories and soil on initial and final concentrations in all P extracts, and on their change during incubation, was assessed using analysis of variance (ANOVA). Where ANOVA showed significant treatment effects, Fisher's protected LSD with a 95% confidence interval was used to identify differences between treatments. All statistical analyses were performed using GenStat 13th Edition (VSN International, 2010).

RESULTS

Influence of soil and P_{init} on extractable P concentration and PBI

Soil and P_{init} concentration significantly affected initial and final PBI ($P < 0.05$) and the initial P concentrations ($P < 0.001$), except for initial $CaCl_2$ -P which was only affected ($P < 0.001$) by soil (Table 5.1). There was also no effect ($P > 0.05$) of P_{init} on the final concentration or change in $CaCl_2$ -P (Table 5.1). Calcium chloride-P concentrations of Soil 3 were large and did not change according to P_{init} , which influenced the overall mean (Table 5.2). There was no effect ($P > 0.05$) of soil or P_{init} on change in Pi and Po after incubation (Table 5.1). Change in Olsen-P was significantly ($P < 0.001$) affected by P_{init} and by soil, while Colwell-P was only significantly ($P < 0.001$) affected by soil (Table 5.1). There was a significant soil by P_{init} interaction with all other initial and final P measures ($P < 0.05$).

Table 5.1. ANOVA F-probability values for the effect of soil, P_{init} concentration, and soil by P_{init} interaction, on the initial, final, and change (Δ) in concentration of various P measures after 418 days of incubation

P extraction	Soil	P_{init}	Soil by P_{init}
Total-P	<0.001	<0.001	<0.001
Initial Po	<0.001	<0.001	0.184
Final Po	<0.001	0.082	0.932
Δ Po	0.093	0.293	0.756
Initial Pi	<0.001	<0.001	<0.001
Final Pi	<0.001	<0.001	<0.001
Δ Pi	0.093	0.293	0.756
Initial $CaCl_2$ -P	<0.001	0.129	0.552
Final $CaCl_2$ -P	<0.001	0.243	0.359
Δ $CaCl_2$ -P	<0.001	0.691	0.942
Initial Olsen-P	<0.001	<0.001	<0.001
Final Olsen-P	<0.001	<0.001	<0.001
Δ Olsen-P	<0.001	0.005	0.679
Initial Colwell-P	<0.001	<0.001	<0.001
Final Colwell-P	<0.001	<0.001	<0.001
Δ Colwell-P	<0.001	0.193	0.057
Initial PBI	<0.001	0.029	0.003
Final PBI	<0.001	0.029	0.001
Δ PBI	<0.001	0.922	0.388

Change in extractable soil P concentrations during incubation

Averaged across all soils and P_{init} concentrations, P_o significantly ($P<0.001$) decreased during incubation (Table 5.2) whilst P_i , $CaCl_2$ -P, Colwell-P, and PBI significantly ($P<0.001$) increased (Table 5.2). The magnitude of the overall increase in P_i , which ranged from 49 mg/kg in Soil 3 to 211 mg/kg in Soil 5 (Table 5.2), was approximately 10-30 times greater than the mean increases in $CaCl_2$ -P, Olsen-P and Colwell-P. However, for Soil 3, more than 100% of the increase in P_i was measured by the Colwell extract, while increases in Olsen-P and $CaCl_2$ -P concentrations were only 18 and 13 mg/kg lower than the P_i increase (Table 5.2).

The $CaCl_2$ -P increase, indicated by $\Delta CaCl_2$ -P in Table 5.2, for Soil 3 was significantly ($P<0.001$) higher than the increases measured for all the other soils. The increase for Soil 3 was over 400-fold greater than the increase for Soil 1, which had the smallest increase (Table 5.2). In addition, $CaCl_2$ -P increased significantly ($P<0.001$) between 0 and 38 days for Soils 3 and 6, and between 38 and 114 days for Soil 3 (Figure 5.1), remaining steady thereafter. The increase ($P<0.001$) in Olsen-P for Soil 3 was significantly ($P<0.001$) different to the change for all the other soils (Table 5.2). Similarly, an increase in Colwell-P ($P<0.05$) occurred for Soils 3 and 6, compared to the other soils which decreased (Table 5.2). The decreases in PBI of Soils 1 and 5 were significantly ($P<0.05$) different to the increases for the remaining soils (Table 5.2).

Table 5.2. Mean initial P concentrations (mg/kg) and their change (Δ) during the 418 day incubation across all soils and P_{init} concentrations, for individual P_{init} concentrations across all soils, and individual soils across all P_{init} concentrations

	Initial P_t	Initial P_i	ΔP_i	Initial P_o	ΔP_o	Initial $CaCl_2$ -P	Δ $CaCl_2$ -P	Initial Olsen-P	Δ Olsen-P	Initial Colwell-P	Δ Colwell-P	Initial PBI	Δ PBI
P_{init}	Across all soils												
1	681a	166a	77a	515a	-77a	4.65a	5.68a	24.6a	8.5a	63a	11a	249c	23a
2	717a	215b	86a	502a	-86a	6.39a	7.66a	30.2b	7.0a	77a	14a	239bc	43a
3	778b	228b	128a	550a	-128a	6.72a	4.55a	44.6c	2.4ab	115b	13a	204ab	34a
4	1049c	366c	151a	682b	-151a	9.23a	5.86a	78.4d	-3.9b	237c	1a	193a	34a
Soil	Across all P_{init} concentrations												
1	1454a	472a	118a	982a	-118a	0.18a	0.07a	39.8a	-4.0ab	167a	-7ab	561d	-39a
2	665b	188b	97a	477b	-97a	0.32a	0.17a	38.9a	-6.2a	128b	-19a	197b	40b
3	222c	47c	49a	175c	-49a	26.24b	31.07b	45.3a	36.2c	51c	61d	13a	116c
4	515d	152b	103a	362d	-103a	1.03a	0.47a	41.4a	-1.0ab	125b	3b	52a	92bc
5	1518e	496a	211a	1022a	-211a	0.12a	0.25a	31.0c	3.6b	145d	-8ab	470c	-110a
6	464d	109b	86a	355d	-86a	12.62c	3.58a	70.5d	-7.7a	123b	27c	34a	90bc

Letters that are different within columns denote significant ($P<0.05$) differences between P_{init} concentrations across all soils, and between soils across all P_{init} concentrations, respectively.

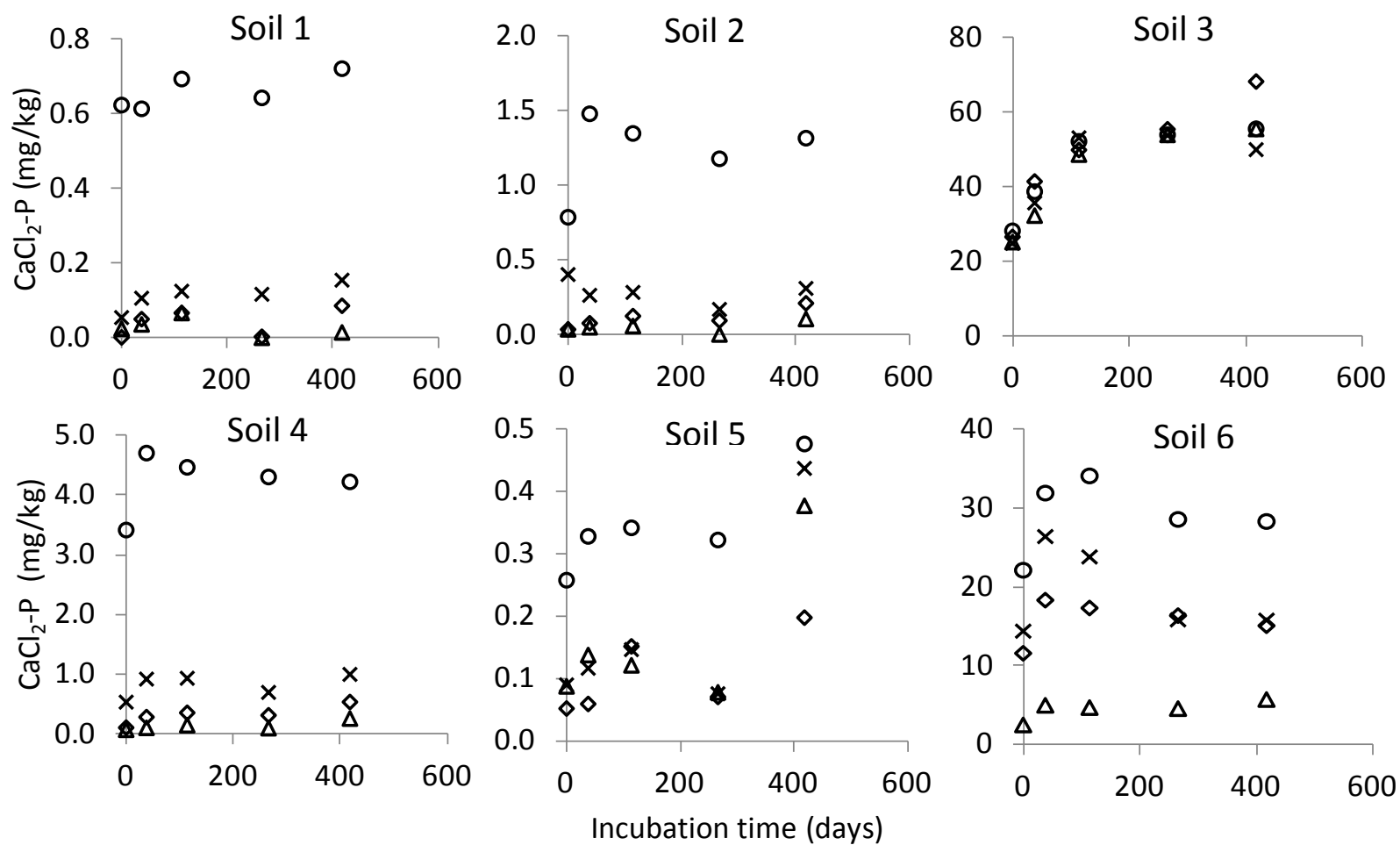


Figure 5.1. Mean changes in $\text{CaCl}_2\text{-P}$ concentrations during the incubation (418 days) for each soil and P_{init} concentration: 1 (Δ), 2 (◊), 3 (x) and 4 (O). Note the different scales of the y-axes.

Contribution of soil drying before extraction to changes in CaCl₂-P concentrations

Overall, the CaCl₂-P concentrations of the soil dried directly before extraction were greater ($P<0.05$) than those of the soils which were not dried directly before extraction i.e. kept constantly moist since incubation. The CaCl₂-P increases after DRW for Soils 3 (4.90 mg/kg) and 6 (5.65 mg/kg) were greater ($P<0.05$) than those for the other soils. However, these increases for Soils 3 and 6 only represented 21 and 47%, respectively, of the mean increase in CaCl₂-P after 114 days, which was when maximum CaCl₂-P was reached for Soil 6 and CaCl₂-P increases slowed for Soil 3 (Figure 5.1). In contrast, CaCl₂-P concentrations of Soils 1 and 5 were slightly higher for the constantly moist soils (0.02 and 0.05 mg/kg, respectively).

DISCUSSION

After DRW, the CaCl₂-P concentrations of the lowest PBI soil (Soil 3) continued to significantly ($P<0.001$) increase for up to approximately 144 days, by which time mean concentrations doubled and were near 50 mg/kg. Such an increase would supply ample P for plant uptake and significantly increase the risk of environmental P loss (McDowell *et al.*, 2001b). This suggests that coarse-textured soils with high OM contents, such as the Podosol Soil 3, are at great risk of environmental loss after DRW cycles. Thus, microbial and physico-chemical changes due to DRW may further exacerbate the inherent P loss risk for very low and extremely low PBI soils.

Sparling *et al.*, (1985) suggested that microbial death after drying contributed between 0.4-15.8 $\mu\text{g P/g}$, which was 4-76% of Olsen-P measured for a range of 15 New Zealand pasture soils sampled to 50 mm. The increase in CaCl₂-P concentrations measured when comparing soil which had been dried and rewet with extraction solution at the conclusion of our incubation, with soil which was constantly moist, suggests that it is unlikely microbial cell lysis contributed the entirety of the released Pi. However, a larger flush of microbial P may have occurred during incubation because soils were rewet with water for between 1 and 418 days before P was extracted. Thus, there was a greater period for mineralisation of the released microbial-P (Brookes *et al.*, 1982) and OM, when compared to only 30 minutes for the soils rewet with CaCl₂ during extraction. In addition, Turner *et al.*, (2003) suggested that, compared with water, extraction with dilute salt solutions such as 10 mM CaCl₂ was unlikely to induce sufficient osmotic shock for cell lysis. The comparison of DRW and continuously moist soils of the current study indicates that extraction with CaCl₂ increases P concentrations, thought to be partly due to osmotic shock and cell lysis. Indeed, Grierson *et al.* (1998) reported that between 4 and 5 mg P/kg was extractable in KCl within one day of rewetting a soil in which P sorption was considered inconsequential. The increases measured by CaCl₂ extraction in the current study may not have been as large as those which may have occurred if extracted with water. However, even if CaCl₂-P concentrations of DRW soils were ten times greater, they would not have been large enough to account for the increase in Pi observed during incubation. Indeed, CaCl₂-P concentrations of Soils 1 and 5 did not increase at all after DRW, when compared to the continuously moist samples. This is thought to be due to the higher clay, OxAl, and OxFe content, and thus, greater PBIs and P sorption capacities of Soils 1 and 5, which were a Ferrosol and Dermosol, respectively,, compared to the Podosol and Hydrosol (Soils 3 and 6).

Turner *et al.*, (2003) reported reactive-P to be lower for dried samples than constantly moist samples of two high-P sorbing soils. The decrease in PBI observed in the current study for the two highest PBI soils is consistent with the suggestion of Turner *et al.*, (2003) that the difference was the result of re-sorption of released microbial-P. Thus, sorption of released P decreased the overall capacity of the soil to sorb more P. Indeed, when total microbial-P is measured using fumigation, a parallel P spike is included to correct for this sorption of released microbial-P (Brookes *et al.*, 1982). Microbial-P sorption corrections for high sorbing soils of 16 to 21 mg/kg have been reported (Morel *et al.*, 1996). Thus, sorption of some of the released P during incubation and extraction may have restricted corresponding increases in CaCl_2 -P and Olsen-P concentrations in high PBI soils, in spite of these soils measuring the largest total P_i increases.

Generally, only a small proportion of the P_i increase during the incubation was extractable by CaCl_2 and NaHCO_3 . However, for Soil 3 the increase in CaCl_2 -P during incubation accounted for the majority of the P_i released. This measurable increase in solution P concentration was probably because its extremely low P sorption capacity limited the re-sorption of desorbed, solubilised, and mineralised P. Oehl *et al.*, (2001) and Grierson *et al.*, (1998) observed limited sorption following microbial-P release in soils with low sorption capacity. However, the increase in Colwell-P for the two soils with the lowest PBI (Soil 3 of 61 mg/kg and Soil 6 of 27 mg/kg) suggests that some P was weakly sorbed, despite their PBIs increasing due to desorption during incubation. Although it is acknowledged that single extractions only provide a snapshot of P availability, the changes in total P_i , P_o , PBI, and extractable P, highlight the importance of these measures to aid our understanding of the fate of the released P.

We hypothesise that P released through cell lysis and mineralisation, and OM solubilisation and mineralisation, which occurs upon DRW, was taken up through various physico-chemical and biological processes soon after release. Several researchers (Brookes *et al.*, 1982; McLaughlin *et al.*, 1986; He and Zhu, 1997) have reported that microbial cell lysis released approximately 40-66% of microbial-P into extracting solutions. Thus, not all microbes are killed during DRW, meaning some of the released P may have been rapidly hydrolysed (Brookes *et al.*, 1982) and taken up by surviving microbes (Grierson *et al.*, 1998) during CaCl_2 -P, NaHCO_3 -P, and PBI extraction, since no chloroform was used.

In the absence of plant uptake, it is possible that microbial uptake of P during incubation may have generated a concentration gradient which could have led to soil P desorption and the measured increase in PBI. However, we suggest it is impossible that the microbes would have contained the mean 318 mg/kg which was desorbed. Although variable, the microbial biomass of grassland soils has been reported to only constitute less than 10% of P_t (Oberson and Joner, 2005). This would mean that between 16 mg P/kg (Soil 3) and 114 mg P/kg (Soil 5) was contained within microbes in the current study. These concentrations are in line with the range of 4 to >100 mg/kg summarised by Oberson and Joner (2005) for six grassland soil studies, but much less than the mean concentration of desorbed P (318 mg/kg) of this study. Nevertheless, microbes may have limited the sorption of released P as microbes can effectively compete with plants for soil solution P (Richardson and Simpson, 2011). Indeed, microbes represent a significant pool of immobilised P that is temporarily unavailable

to plants and soil sorption. An alternative cause of the increased PBI may be physico-chemical reactions caused by the DRW cycle.

Phosphorus released to the soil solution may be precipitated, adsorbed to sesquioxide surfaces, and/or absorbed into sesquioxide matrices through solid state diffusion. While P sorption capacity has been reported to increase due to drying (Barrow and Shaw, 1980), it has also been reported to return to that of continuously moist soil after 6 to 12 months of moist incubation (Haynes and Swift, 1985). Thus, it is unlikely that drying would have directly contributed to the increases in PBI in the current study. However, during incubation, some already sorbed P may have moved from loosely to strongly held forms, including inside soil particles (absorption) (Barrow, 1983a). Although not measured in the current study, change in pH and ionic strength are mechanisms that have been reported to contribute to desorption (He and Zhu, 1997; Celi *et al.*, 2003). Desorption of Po to replenish the soil solution after microbial withdrawal of Pi, and solubilisation of previously sorbed OM (Haynes and Swift, 1985; Magid and Nielsen, 1992; Turner and Haygarth, 2003; Wu and Brookes, 2005; Butterly, 2008) may have also contributed to PBI increases. Soluble OM may also originate from microbial cells killed during drying. Thus, it is suggested that a change in OM solubility released some incorporated Po, which may have been hydrolysed by micro-organisms, contributed to the Pi increase in the current study (Tables 5.1 and 5.2) since the soils had been dried before and after incubation. This is in line with the increase in Pi and decrease in Po independent of soil and P_{init} concentration, suggesting the mechanisms were consistent across all soils.

CONCLUSION

In addition to physico-chemical changes, this study is consistent with the prevailing view that microbial cell osmotic shock and lysis, and OM and Po solubilisation and mineralisation, after DRW may contribute to increases in Pi. However, only a small amount of the released Pi was generally extractable by CaCl_2 or NaHCO_3 . We hypothesise that the availability of the released P is reduced by sorption, physico-chemical processes caused by soil drying such as absorption and precipitation, and immobilisation within microbes that survive DRW. Thus, we conclude that increases in Pi after DRW may not be of agronomic or environmental significance for most soils. However, increases in Pi after DRW may persist for a significant period of time for soils with very low to extremely low PBI, due to their limited sorption capacities, further exacerbating their inherent risk of P loss. For such low PBI soils, the addition of amendments to increase their P sorption capacity is warranted.

6

**RECOVERY OF SURFACE APPLIED PHOSPHORUS FERTILISER WITHIN THE SURFACE
100 CM OF TWO PASTURE SOILS WITH CONTRASTING SOIL PHOSPHORUS
SORPTION CAPACITIES**

ABSTRACT

The leaching of applied fertiliser phosphorus (P) for the plant root zone is an inefficient use of a finite resource. The current study compared two grazed pasture soils which represent the extremities in P buffering indexes (PBI) of soils used for dairy pasture production in Australia. Each soil had previously received split applications of either 500 or 1644 kg P/ha as triple superphosphate according to their PBI. An attempt to recover the applied P was made 5.5 years after the final fertiliser application by sampling to a depth of 100 cm, with soil split into 6 depth intervals (0-5, 5-10, 10-20, 20-30, 30-50 and 50-100 cm), and analysed for total-P (Pt) and bulk density to estimate P loadings (kg/ha). After accounting for P export in animal product, and an increase in standing pasture P concentration, only 94 kg P/ha, or 19%, of the 500 kg P/ha applied was recovered in the surface 100 cm of the extremely low PBI Soil 3, and 944 kg P/ha, or 57%, of the 1644 kg P/ha applied was recovered from the higher PBI Soil 1. Some of the disparity could have been due to the low sensitivity of the Pt method. After accounting for an error of 10% in Pt, half of the P applied to Soil 3 was still not recovered, suggesting that it was lost from the sampling zone. In addition, Soil 3 had extremely high $\text{CaCl}_2\text{-P}$ concentrations in the surface 10 cm, indicating that it required less added P to increase the risk of P loss than Soil 1. This suggests that fertilising extremely low PBI soils poses a significant risk of surface and subsurface P losses, presumably due to the lack of available P sorption sites.

INTRODUCTION

The movement of phosphorus (P) from soil to groundwater and surrounding waterways is an issue of international environmental concern (Sharpley *et al.*, 1987). Also of concern is the potentially finite supply of P (Cordell *et al.*, 2009); necessitating efficient fertiliser use. The sustainability of applying P fertiliser to soils with low P buffering indices (PBI) and high environmental P concentrations is questionable, from both environmental and economic perspectives, since such soils are at high risk of P movement. Although the P can accumulate at depth where soil texture becomes finer and/or PBI increases, grazed pasture species source 40% of their P from the surface 10 cm, and 80% from the surface 30 cm (Crush *et al.*, 2005). Thus, accumulation of P beyond the plant root zone effectively represents a loss of P from the pasture cycle. Additionally, P can be lost from the soil subsurface through leaching into ground water, or through lateral flow into watercourses.

Phosphorus loss can be quantified by direct measurement of P in surface runoff or via leaching with lysimeters. However, such experiments can be time consuming and expensive. Alternatively, changes in soil total P (Pt) can be used to infer P loss. Applied P which is not recovered in – the soil through measurement of Pt, the standing pasture, or exported product – is assumed to be lost from the sampling depth or to the surrounding environment. The application of 500 kg P/ha to a Podsol (Atterberg, 1905; Isbell, 2002) with an extremely low PBI resulted in little increase in Olsen-P concentrations in the surface 10 cm, viz. from 13 to 19 mg/kg (Chapter 2). The extremely low PBI and small increase in extractable P suggests that the P is unlikely to have been sorbed and may have been lost, not only from the pasture cycle but the soil entirely. However, recovery of the applied P to a depth greater than measured in Chapter 2 is required to better assess whether the applied P was indeed lost or simply moved beyond the surface 10 cm.

Low P recoveries from soils of low P sorption capacity have previously been reported (Russell, 1960; Ozanne *et al.*, 1961; Lewis *et al.*, 1987). Lewis *et al.*, (1981) reported up to 100% loss from the surface 30 cm of siliceous sands after applying up to 80 kg P/ha. The majority of studies have hypothesised that the unrecovered P moved beyond their sampling depths, which were typically within the surface 40 cm (McCaskill and Cayley, 2000; Burkitt *et al.*, 2004b). Indeed, Bryan (1933) reported P leaching to depths of at least 90 cm in heavily fertilised (150-300 kg P/ha.yr) deep sandy soils. Thus, sampling to at least 100 cm is necessary on very sandy soils to recover P that may have accumulated further down the soil profile.

Factors which have been reported to influence the downward movement of P include; soil P sorption capacity (Cox *et al.*, 2000) as estimated by measures such as oxalate-extractable iron (OxFe) and oxalate-extractable aluminium (OxAl) (Lewis *et al.*, 1981) and PBI (Burkitt *et al.*, 2004a); organic matter (OM) content (Russell, 1960; Ozanne *et al.*, 1961; Lewis *et al.*, 1981); and transport mechanisms such as preferential flow via cracks and macropores (Cox *et al.*, 2000). In addition, high surface soil P concentrations have been reported to increase P movement when compared to lower soil P concentrations (Hesketh and Brookes, 2000; McDowell and Sharpley, 2001), due to a greater occupancy of P sorption sites.

The objective of the current study was to: 1) assess the influence of soil texture and PBI on downward P movement by comparing two contrasting soils which had both received either a split application of a large quantity of P fertiliser, or zero fertiliser (control), 2) recover P from within the soils surface 100 cm, which was divided into 6 depth intervals, and 3) use various soil P extracts to compare P recoveries according to soil, depth and P fertiliser treatment.

MATERIALS AND METHODS

Site management and soil characterisation

Two field sites of soils with contrasting P sorption capacity were selected from those established in 2005 and described in Chapter 2. Briefly, Soil 1 was a red Ferrosol (Atterberg, 1905; Isbell, 2002) with clay loam surface (10 cm) texture, while Soil 3 was a semi-aquic Podsol (Atterberg, 1905; Isbell, 2002) with sandy loam/peat surface texture (Tables 2.1 and 6.1).

Both soils were located within non-irrigated grazing properties in north-west Tasmania, Australia. Mean annual rainfall was 1450 mm for Soil 1 and 1069 mm for Soil 3 (Bureau of Meteorology, 2012a). Both soils supported perennial pasture and were grazed rotationally at varying stocking rates by dairy heifers for Soil 1 and beef cattle for Soil 3. Phosphorus exports in animal products were not directly measured for each soil. Instead, P exports were estimated by combining pasture P concentrations and removal based on research in north-west Tasmania by Cotching and Burkitt (2011), and Burkitt *et al.*, (2010a), and whole farm nutrient budgets.

Treatments and soil sampling

To examine P movement between depths for each soil, plots from the zero (control) and highest P fertiliser treatments, with three replicates, were selected from the original study described in Chapter 2. The final P fertiliser application occurred 5.5 years prior to the deep soil sampling of the current study. The high P plots had received split applications of triple superphosphate (20% P, 14% Ca, and 1% S) 12 months apart totalling 1644 kg P/ha for Soil 1 and 500 kg P/ha for Soil 3.

Five soil cores (150 cm deep x 3.7 cm diameter) were taken randomly across each site with a hydraulic corer to characterise the soil profile (Table 6.1). The soil characterisation depth was 50 cm greater than used to measure P recovery so any change in soil in close proximity to our maximum sampling depth could be identified.

Bulk density (BD) was estimated by sampling five cores to a depth of 100 cm randomly within the buffer zone between treatment blocks. Only cores that were extracted intact and without obvious signs of compaction were used. Bulk density was estimated for the depth intervals of 0-5, 5-10, 10-20, 20-30, 30-50 and 50-100 cm by cutting the cores at these measurements and weighing the soil after oven drying at 105°C for 72 h. For Pt measurement, ten 100 cm soil cores were sampled randomly from within each plot replicate,

avoiding the outer edges to minimise contamination from neighbouring plots. Each core was cut as per the depth intervals used for BD and bulked according to depth and replicate plot. These intervals accommodated soil texture boundaries as identified in Table 6.1, and sample depths used for common agronomic and environmental P tests for pasture soils. Bulked soils were oven dried at 40°C for at least 48 hrs and ground to pass through a 2 mm sieve. Pasture species roots were fine and evenly distributed, and were not removed from any of the soil samples.

Chemical analyses

Soil samples for P measurement were analysed for calcium chloride extractable-P (0.01 M CaCl₂) (Houba *et al.*, 2000), oxalate extractable-P (Ox-P) (Schwertmann, 1964), and Kjeldahl Pt concentrations (Sommers and Nelson, 1972), and the unadjusted P buffering index (PBI) (Burkitt *et al.*, 2008).

Fertiliser phosphorus recovery

The mean weight of soil per plot for each depth interval was calculated from BD, enabling the quantity of P (kg/depth interval/plot) to be calculated using the corresponding Pt concentration. Total-P measured to 100 cm was obtained by summing the quantities measured for each depth interval. Phosphorus recovery was calculated as the difference between Pt (kg P/ha) measured to a depth of 100 cm in the P fertilised soil and the unfertilised soil, and was expressed as a percentage of the quantity of P fertiliser applied, after accounting for differences in P export and standing pasture P concentration.

Statistical analyses

Analysis of variance (ANOVA) was used to assess the significance of changes in CaCl₂-P, Ox-P, and Pt concentrations, and PBI, by including P fertiliser treatment and depth, and their interaction, as categorical variables blocked by replicate for each soil. Where ANOVA showed a significant effect, Fisher's protected least significant difference (LSD) with a 95% confidence interval was used to identify differences between P fertiliser treatments and depths. Linear regression was used to examine the relationship between soil P extractions across all depths. All statistical analyses were performed using GenStat 13th edition (VSN International, 2010).

Table 6.1. Profile descriptions, to a depth of 150 cm, of the two contrasting soils from north-west Tasmania

Horizon	Depth	Colour [†]	Texture [‡]	Structure
<i>Soil 1 Red Ferrosol</i>				
A1	0-15	7.5YR 2.5/3	light clay loam (LCL)	moderately developed
A3	15-27	7.5YR 3/4	clay loam (CL)	strongly developed
B1	27-72	7.5YR4/4	light clay (LC)	strongly developed
B21	72-110	5YR 4/6 & 2.5YR 3/6 few prominent mottles	light medium clay (LMC)	strongly developed
B22	110-150	7.5 4/6	medium clay (MC)	strongly developed
<i>Soil 3 Podsol</i>				
A1	0-7	10YR 2/1	sapric peat (AS)	weak
A12	7-32	2.5YR 2.5/1	loamy sand (LS)	weak
A21	32-43	2.5Y 4	loamy sand minus (LS-)	massive
A22	43-57	2.5Y 5/2	sand (S)	massive
Bh	57-63	2.5Y 3/1	silty loam (SL)	massive
B2	63-86	2.5Y 5/3	silty light clay subplastic (SLC)	massive
B3	86-102	2.5Y 4/2	sandy clay loam (SCL)	massive
2D1b	102-120	2.5Y 5/6	light clay (LC)	weak
2D2b	120-150	2.5Y 7/1 & 2.5Y 6	light clay (LC)	weak

[†]Munsell Colour (Munsell, 1966), [‡]International Soil Texture Classification System (Atterberg, 1905; Isbell, 2002).

RESULTS AND DISCUSSION

Soil characterisation

The sorption capacities measured in the surface 10 cm varied greatly between the two sites with OxAl and OxFe contents of 5900 and 4700 mg/kg for Soil 1, and 300 and 800 mg/kg for Soil 3, with PBI being 519 and 6, respectively (Table 2.1). Before P fertiliser application, Soil 1 had the greatest Pt and Po concentrations, while Soil 3 had the greatest organic carbon (OC) content (Table 2.1). Soil 1 was moderately acidic (pH_{CaCl2} 5.4) while Soil 3 was very acidic (pH_{CaCl2} 3.9) (Table 2.1). Soil 3's low OxAl and OxFe content, extremely low PBI, and high OC content within the pasture rooting zone, suggests a low ability to retain P. Based on these characteristics, P which is held in Soil 3 would be expected to be in a readily available form and prone to movement beyond 10 cm under the prevailing climate.

Change in bulk density with depth

For both soils, the BD generally increased with depth (Table 6.2). Due to the high OM content of the surface 10 cm of Soil 3 (OC = 114 g/kg), its BD was lower than that of Soil 1 (OC=95 g/kg). The BD of the surface 5 cm was low for both soils; 0.70 for Soil 1 and 0.32 for Soil 3 (Table 6.2), with respective standard deviations of 0.09 and 0.02, and were consistent with BDs previously measured for these soils (Kidd, *pers. comm*). For depths greater than 10 cm, Soil 3 had greater BD than the Soil 1 (Table 6.2). The greater BD of Soil 3 was due to its massive and weak structure, meaning there was less air-space between the denser sand material than the strongly developed Soil 1 (Kidd, *pers. comm*). The high BD of 2.07 units for Soil 3 which was measured in the 30-50 cm increment, encompassing the lower A2 is consistent with observations that this layer is often very dense, almost cemented, with a perched water table occurring above the Bh (57-63 cm) in wetter months (Kidd, *pers. comm*). Phosphorus movement beyond the Bh horizon would not be expected in this case, with lateral movement of P in water more likely.

Total soil P recovery (%)

Despite sampling to 100 cm in the current study, the P recoveries calculated using mean Pt concentrations were some of the lowest reported in the literature. After accounting for P export, only 57% and 19% of the 1644 and 500 kg P/ha applied to Soils 1 and 3, respectively, was recovered (Table 6.2). Burkitt *et al.*, (2004b) reported P recoveries of 45-57% within the surface 40 cm for a high PBI (939) clay soil which received up to 280 kg P/ha as a single application, which were comparable to that recovered for Soil 1 over 100 cm (57%). The 19% P recovery for Soil 3 was lower than some previously reported recoveries for low P sorbing soils (Russell, 1960; Ozanne *et al.*, 1961; Burkitt *et al.*, 2004b). Although 0% P was recovered from the surface 30 cm of some siliceous sands after applying up to 80 kg P/ha (Lewis *et al.*, 1981), we measured a greater quantity of unrecovered P (406 kg P/ha) over a greater sampling depth.

Soil heterogeneity in Pt, both vertically and horizontally, was suggested by Burkitt *et al.*, (2004b) for their range in Pt concentrations. This would not have been improved through the relatively narrow diameter of the cores (3.7 cm) of the current study, although the 10 samples taken per plot would have limited this spatial error. Compared to the range reported across all soils by Burkitt *et al.*, (2004b) of 11 to 108%, our CV% values were smaller and the range tighter for Soil 1 (1 to 14%), although the range was large for Soil 3 (1 to 91%) (Table 6.2). Like Burkitt *et al.*, (2004b), who measured Pt by digesting soil in nitric and perchloric acids, we question the accuracy of the P recovery approach. Even McCaskill and Cayley (2000) who recovered 93% of applied P suggested that there was a large error in calculated recovery.

The Pt extraction is one potential source of error. The Kjeldahl method, which we used for the current study, is considered to provide 'pseudo-totals' lower than the true value (Rayment and Lyons, 2011). Taylor (2000) reported a correlation between Pt by the Kjeldahl method and Pt by both NaOH fusion and dry ashing, although the Kjeldahl method gave results approximately 3.7% lower than the other methods. If an interaction between added P load and extraction efficiency occurs, the Kjeldahl method may have underestimated the

concentrations of the fertilised soils, resulting in lower recoveries. Further work relating Kjeldahl P with soil P load is required to test this theory. If this is an issue of concern, it may have been exacerbated by the addition of two large quantities of P fertiliser. However, P recovery has been reported not to be affected by the quantity of P applied when determined by digestion for 4 h with boiling hydrochloric acid after washing with magnesium acetate (Russell, 1960; Ozanne *et al.*, 1961; Lewis *et al.*, 1981). If Kjeldahl P concentrations had an error potential of +/-10%, recoveries would have ranged from -14 to 121% for Soil 1, and -39 to 47% for Soil 3. While all of the applied P could potentially be accounted for in Soil 1 by an error of 10% in P, only half of that applied to Soil 3 could be accounted for. This suggests that there are other sources of error in recovering P from Soil 3, or that the unrecovered P was lost from the sampling zone. Approximately 3.4 and 1.1 kg P/ha.yr was estimated to be exported in animal products from the P treated Soils 1 and 3, respectively, than the control. This totalled 22 and 7 kg P/ha over the 6.5 years between the first of two P fertiliser applications at site establishment, and deep soil core sampling. However, this exported P only equated to 1% of that applied to Soils 1 and 3. An estimate of the P content of the standing pasture of the control and fertilised treatments of 0.22 and 0.56% for Soil 1, and 0.29 and 0.30% for Soil 3, respectively, was based on the linear regressions presented by Burkitt *et al.*, (2010a). Assuming there was 30 days of pasture growth upon sampling (0.6 and 1.2 t DM/ha, according to treatment for Soil 1), a difference of 50 kg P/ha (3%) could be accounted for in the standing pasture between treatments for Soil 1. No difference in standing pasture P concentration was estimated for Soil 3 due to the limited change in Olsen-P of the surface 10 cm. Both differences in P export potential and standing pasture P concentration were included in P recovery calculations for the surface 10 cm (Table 6.2). Surface runoff losses of up to 10 kg P/ha.yr have been reported from Australian soils (Nash *et al.*, 2000; Holz, 2007). Thus, potential surface runoff may have accounted for at most 65 kg P/ha of the unrecovered P of these two soils (4 and 13% for Soils 1 and 3, respectively) if it occurred for the fertilised treatment only. However, surface runoff was not included in the P recovery since differentiation in estimated losses between treatments could not be made. However, despite Olsen-P concentrations of Soil 3 not increasing greatly, CaCl₂-P of the fertilised treatment was still ~10 mg/kg greater than the control treatment 6.5 years after the initial P fertiliser application. This suggests that the fertilised treatment of Soil 3 was at greater risk of P loss through surface runoff, and that some of the unrecovered P may have been lost through this mode.

Table 6.2. Mean bulk density and phosphorus recovery (% and kg P/ha) according to sampling depth

Depth (cm)	Bulk density (g/cm ³)	P recovery (%)	Mean recovery (kg P/ha)
<i>Soil 1</i>			
0-5	0.70	29 (9)	482 [†]
5-10	0.95	18 (3)	302 [†]
10-20	0.83	0 (1)	4
20-30	0.95	5 (2)	81
30-50	1.03	5 (14)	75
50-100	1.25	0 (1)	0
0-100	0.95	57	944
<i>Soil 3</i>			
0-5	0.32	9 (1)	42 [†]
5-10	0.61	7 (0)	32 [†]
10-20	0.85	0 (0)	0
20-30	1.37	0 (2)	0
30-50	2.07	5 (91)	25
50-100	1.77	-1 (38)	-5
0-100	1.17	19	94

Mean P recovery was calculated as the difference between the fertilised and control treatments (kg P/ha), which was divided by the quantity of P applied to calculate P recovery percentage. [†]Phosphorus recovery was calculated including a difference in P exported in animal product between treatments of 22 and 7 kg P/ha for Soil 1 and 3, respectively, and an additional 50 kg P/ha in standing pasture for the P fertiliser treated Soil 1. Value in brackets is the CV%.

Influence of soil, P fertiliser treatment, and depth on extractable soil P concentration, PBI, and P recovery (%)

For Soil 3, the majority of the P which was recovered was contained within the 0-10 cm and 30-50 cm intervals, with no P being recovered between 10 and 30 cm (Figure 6.1 and Table 6.2). The high OM content of the surface 7 cm (sapric peat) potentially contributed to the surface recovered P. There was no significant ($P>0.05$) difference in Pt or Ox-P concentration, or PBI, between the P fertiliser treatments for any depth interval (Figure 6.1). Only CaCl₂-P concentrations of the surface 5 cm of Soil 3 increased ($P<0.05$) after P fertiliser application. Assuming historical P fertiliser application before trial site establishment did not saturate the P sorption sites, the extremely low PBI of Soil 3 for the majority of the profile was the most likely reason for the high loss of applied P.

The PBI of Soil 3 only increased ($P<0.05$) for the 50-100 cm interval due to a change in soil texture from sand to silty loam of the A and B horizons at 57 cm (Table 6.1). Even then, the PBI of the 50-100 cm interval of Soil 3 was very low i.e. ~70. We hypothesise that due to the increase in PBI, and the less permeable

B horizon beyond 57 cm, Ox-P and Pt accumulated within the sandy surface 7 cm of the 50-100 cm interval, resulting in their concentrations not being different to those measured in the 5-10 cm interval (Figure 6.1). However, since there was no significant ($P>0.05$) difference in P concentrations within the 50-100 cm interval, irrespective of whether P fertiliser was applied, no applied P was recovered at this depth (Table 6.2). This suggests that the P concentrations of the 50-100 cm interval, or perhaps more actually the surface 7 cm on this sampling interval, may have been the result of historical P fertiliser application, or lateral movement of P between treatment plots.

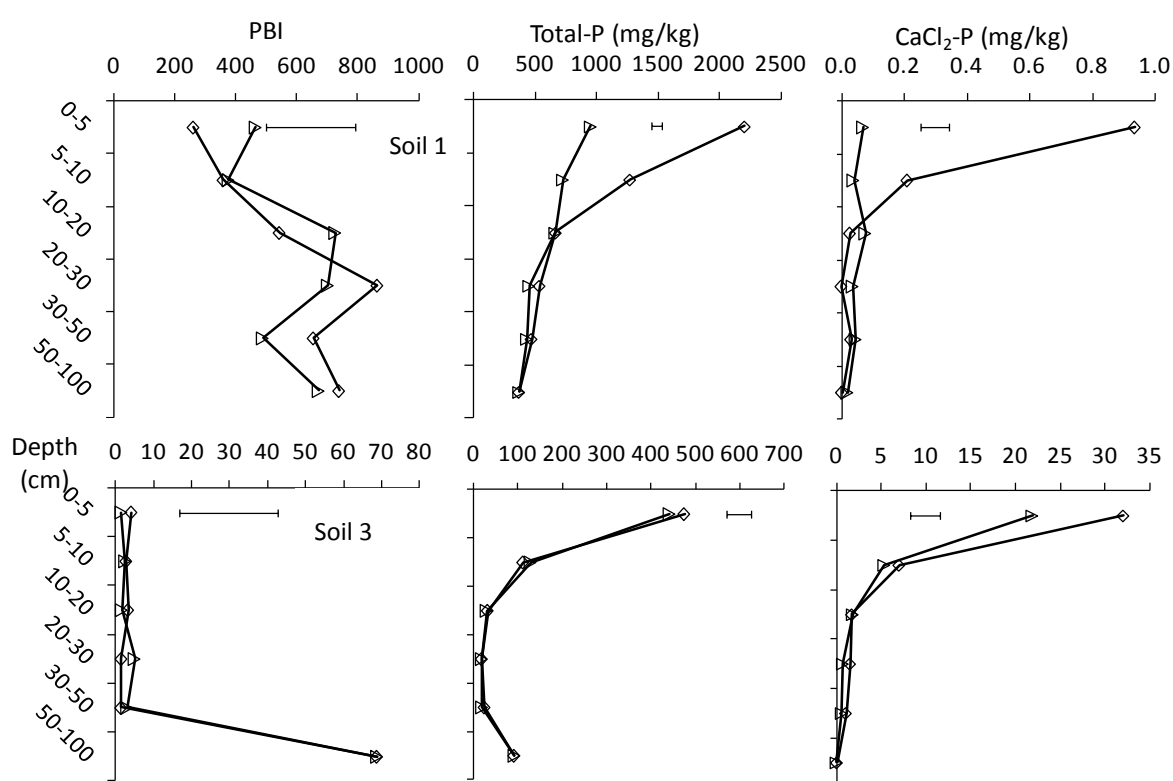


Figure 6.1. Mean changes in PBI, and CaCl₂-P and total-P (mg/kg) concentrations with depth for Soil 1 (top) and Soil 3 (bottom) for the P fertilised (◊) and control (Δ) treatments. Horizontal bars represent the LSDs ($P=0.05$) for the depth by fertiliser P interaction for each soil and extraction method. Note y-axes are variable between soils and P measures.

The majority (81% or 406 kg P/ha) of the unaccounted for P of Soil 3 was most likely lost through surface runoff and lateral movement of soil water through the extremely low PBI soil above the less permeable B horizon. Indeed, lateral movement has previously been suggested to contribute to high P losses (Lewis *et al.*, 1987; Edwards, 1997). Rainfall within four months of the P fertiliser applications of approximately 650 mm in 2005 and 402 mm in 2006 (Bureau of Meteorology, 2012b) may have aided the movement of applied P. Since Soil 3 was slightly elevated compared to surrounding areas of the paddock, subsurface lateral movement to lower lying areas and artificial drains are likely to have contributed to this unaccounted for P.

For Soil 1, the increase in PBI ($P < 0.05$) with depth limited downward P movement, with $\text{CaCl}_2\text{-P}$ and Ox-P concentrations of the fertilised treatment only being greater ($P < 0.05$) than the control soil to depths of 10 and 20 cm, respectively (Figure 6.1). Indeed, the majority of the applied P recovered was within the surface 10 cm, with mean P recoveries at 0-5 and 5-10 cm being 29 and 18%, respectively (Table 6.2). However, 5% of the applied P was also recovered within each of the 20-30 and 30-50 cm intervals. We hypothesise that P moved to the 20-30 and 30-50 cm intervals through preferential flow. Preferential flow involves water moving via small channels through the profile such as root and worm channels (Jensen *et al.*, 1998). Unlike water moving through the bulk soil, the interaction between the P sorbing surface of these channels and the P in solution is minimised in preferential flow and P loss to subsoils is more likely (Stamm *et al.*, 1998; Cox *et al.*, 2000; Toor *et al.*, 2005). Burkitt *et al.* (2004b) suggested that P moved past their 40 cm sampling zone via macropores such as earthworm holes and soil cracks. This finding questions whether a 3.7 cm diameter soil core can accurately reflect P distribution as the result of water movement, and allow assessment of recovery of the applied P.

In addition to, or instead of preferential flow, P may have moved down the soil profile of Soil 1 as organic P (Po). Heckrath *et al.*, (1995) reported large concentrations of reactive P in drainage from the Broadbalk experiment, despite the large P sorption capacity of the subsoil, and postulated that P may have been transported in less readily sorbed forms, i.e. Po, before conversion to reactive P. Indeed, dissolved Po has been reported to be more vertically mobile, in some soils, than reactive P (Magid *et al.*, 1996; Toor *et al.*, 2003; Murphy, 2007).

Considering the high PBI of Soil 1 and that the site was flat and well drained, it seems highly unlikely that almost half of the 1644 kg P/ha applied had been lost beyond our sampling depth, or through surface runoff. In addition, we measured no change in PBI due to the large application of P fertiliser for either soil, thus, the low P recoveries in the current study were unlikely to be due to the saturation of P sorption sites. This suggests that the applied P was retained by Soil 1, but was not recoverable by the Kjeldahl extraction.

The use of slowly soluble P fertilisers has been shown to reduce P losses from soils prone to P leaching (Ozanne *et al.*, 1961; Gillman, 1973; Weaver *et al.*, 1988), as the P is slowly released over time. In contrast, soluble P fertilisers readily dissolve into the soil solution, and are therefore prone to environmental losses if not taken up by plants straight away. The acidity and high rainfall of Soil 3 is suitable for slow release fertilisers,

as shown through work by Sale *et al.*, (1997). However, runoff losses from slow release fertilisers may still be high where it is applied in surplus to plant requirements. For example, Alston and Chin (1974) reported high runoff losses of P from an Australian Podsol fertilised with unreactive Florida rock. Thus, P application at rates which do not exceed plant requirements or a soils ability to retain P would likely be more important in reducing P losses than the form of P applied. Considering Soil 3 had a relatively short fertiliser history before site establishment i.e. ~20 years, $\text{CaCl}_2\text{-P}$ concentrations of these soils may be naturally high due to mineralisation of the high OM content of the surface 7 cm.

Relationship between the P extractions

From the measurement of P concentrations with depth, it was evident that Soil 3 contained much greater $\text{CaCl}_2\text{-P}$ concentrations than Soil 1, despite Soil 1 having greater Ox-P and Pt concentrations. Thus, further investigation of the relationship between P recoveries, and how the P was held in the soil was required. When linear equations were fitted to the relationships presented in Figure 6.2, r^2 values were > 0.80 ($P < 0.001$).

The slope for Ox-P and Pt of Soil 1 was over five-fold greater than the slope for Soil 3 (Figure 6.2). Compared to Soil 1, Soil 3 showed a much steeper increase in $\text{CaCl}_2\text{-P}$ for both Pt (117-fold) and Ox-P (640-fold) (Figure 6.2). Thus, the extremely low PBI Soil 3 had large $\text{CaCl}_2\text{-P}$ concentrations for a comparatively small concentration of Ox-P and Pt (Figure 6.1). This indicates that Soil 3's inherent extremely low PBI, and OxAl and OxFe content, resulted in P being retained in a more readily extractable form than the P of the high PBI, and high OxAl and OxFe content, Soil 1. Indeed, the $\text{CaCl}_2\text{-P}$ concentrations of the surface 10 cm of Soil 3 were greater than those previously reported in the literature for Australian and international soils (McDowell and Sharpley, 2001; Koopmans *et al.*, 2004; Dougherty *et al.*, 2006; Dougherty *et al.*, 2008; Burkitt *et al.*, 2010b). This suggests there is a greater risk of environmental loss for Soil 3, irrespective of subsequent P fertiliser application, even though surface 10 cm Pt concentrations were only approximately 300 mg/kg. Nair and Harris (2004) utilised similarly problematic soils from Florida, America, when developing a measure to consider risks arising from previous P loadings as well as inherently low P sorption capacity. They argued that a low soil P concentration may not necessarily increase after application of P if the P concentration was low due to the added P being lost due to the soils low P sorption capacity.

This suggests that if these soils are to be sustainably used for agricultural purposes, P retention would need to be increased through addition of amendments such as red mud (Summers *et al.*, 1996), or by increasing pH (Murphy and Stevens, 2010). If PBI was increased through this method, care must still be taken to ensure soil P concentrations were not built beyond that required for optimum pasture production, since fertiliser practice would most likely have the largest impact and be the most cost effective means of reducing P losses. Interestingly, there has been a suggestion that the agronomic P optimum for low PBI soils may be lower than is currently thought (Weaver and Summers, 2010).

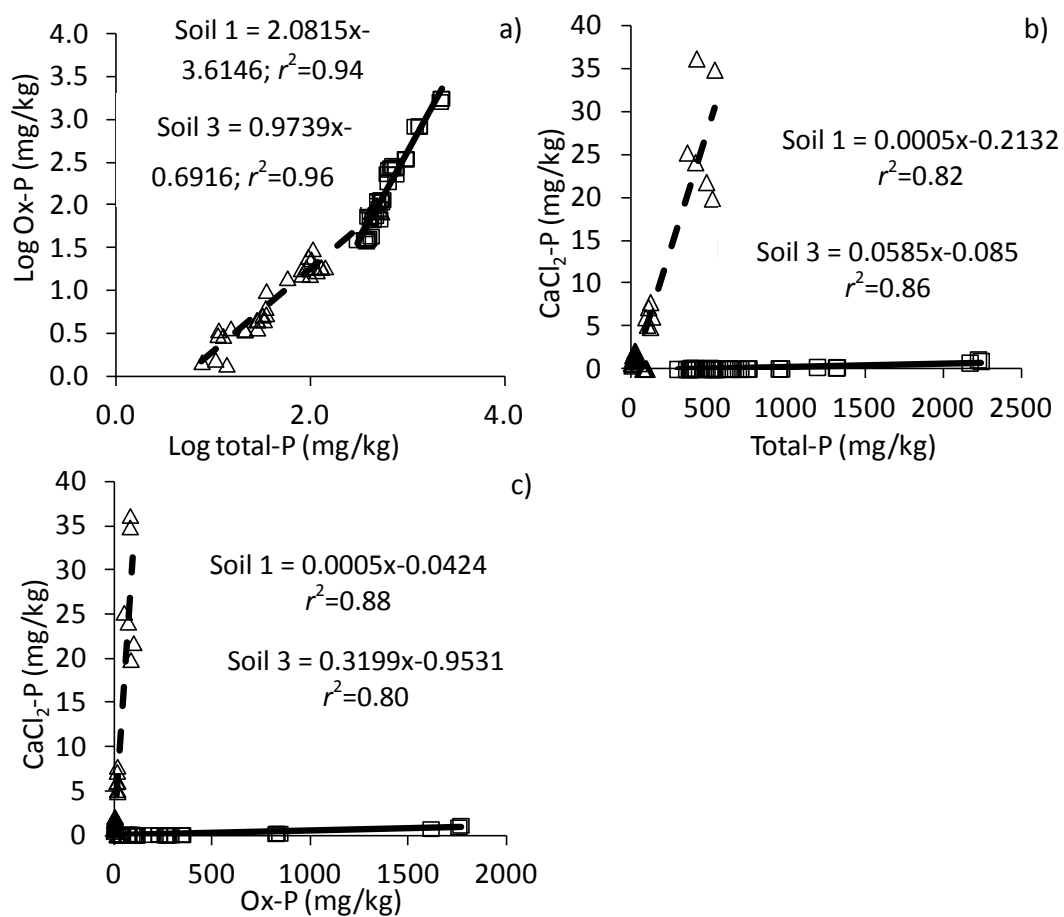


Figure 6.2. Relationship between the P measures and Soil 1 (—□—) and Soil 3(---Δ---). Note: the relationship between Ox-P and Pt was presented on a log-log scale for ease of viewing

CONCLUSION

Several studies, including this study, have been unable to recover all of the P applied. The P recoveries for the two soils of the current study question the accuracy of the Kjeldahl Pt recovery method. Validation of the P recovery approach using Pt is required through comparison with measurement of actual P loss from controlled lysimeter studies, in addition to measurement of other P loss pathways i.e. surface runoff. Determination of the fate of applied P is important to be able to ascertain the environmental impact of fertilising pasture soils.

Even after accounting for an error of 10% in Pt, half of the P applied to Soil 3 was not recovered, and appears to have been lost from the pasture P cycle. This suggests there are large risks associated with applying P fertiliser to extremely low PBI soils. Extremely low PBI soils, such as Soil 3, are used for intensive grazing systems in Australia, and represent a significant risk if not appropriately managed. The extremely high $\text{CaCl}_2\text{-P}$ concentration in relation to the comparatively small Pt concentration in the surface of Soil 3 highlights the risk of using this extremely low PBI soil for agricultural purposes. Even if slow release P fertilisers are used, agronomic optimum soil P concentrations, as currently defined, may not be possible for such soils due to their extremely low ability to retain P. However, there has been suggestion that agronomic optimum may be lower than currently thought for low PBI soils. Irrespective of agronomic optimum, lower risks of environmental loss may be possible for these soils if amendments were applied to increase PBI, and ultimately increase the soils ability to retain P.

OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Sustainable land management requires an understanding of chemical, biological, and physical processes that affect the availability of P in soils. A balance between protection of the environment and sustainable use of P in agriculture is required. Extractable soil P concentrations substantially above the agronomic optimum are costly both financially and environmentally, and put added pressure on a finite supply of raw P.

Reducing excessive P concentrations in pasture soils can be achieved through applying fertiliser P at rates less than that required for maintenance. Decreases in extractable soil P concentrations were observed by comparing a wide range of initial P (P_{init}) concentrations, on-going P fertiliser (P_{fert}) rates, and soil types representative of Australian dairy operations. Greater decreases occurred the higher the P_{init} calcium chloride extractable-P ($\text{CaCl}_2\text{-P}$), Olsen-P, and Colwell-P concentrations, and the lower the on-going P_{fert} . After up to three to four and a half years of withholding P fertiliser, soil P concentrations which were initially well above agronomic optimum remained above this level. Thus, no P related constraints on pasture production would be expected. Of particular importance was the greater proportional decrease of the environmentally available P fraction ($\text{CaCl}_2\text{-P}$) compared to the agronomic P fraction (Olsen-P and Colwell-P). This indicates that, under appropriate circumstances, reducing soil extractable P concentrations may result in a proportionally greater decrease in the risk of environmental P loss, while maintaining plant-available P.

A model was developed to assist policy makers and land managers in setting realistic timeframes to return soils with excessive P to agronomic and/or environmental optimum targets of 17 mg/kg and 0.25 mg/kg, respectively. Since decreases are slow (range from 0 to 135 years), policy makers need to have realistic expectations about achievable P decreases when implementing policy designed to withhold fertiliser for environmental and economic objectives. In addition, land managers can be reassured of the implications of withholding P fertiliser i.e. that soil extractable P concentrations will not 'plummet' over a short period of time. The model predicted that some soils will maintain Olsen-P and Colwell-P concentrations above agronomic optimum with minimal risk of P loss, while other soils will exceed (sometimes many times over) the $\text{CaCl}_2\text{-P}$ environmental threshold, even if they are below agronomic optimum. While the decreases in extractable soil P measured in the current study vary to some degree from those measured in other studies, all studies found that the periods of decrease are likely to be longer than may be deemed acceptable to policy makers, since P losses to the environment would most likely continue whilst soil P measures decrease. To achieve more rapid decreases in excessive soil P concentrations, actively increasing P exports through removing P in plant and animal products i.e. harvesting and removing silage and/or hay, would need to occur in addition to withholding P fertiliser application. The following are recommended for future research:

- incorporate into the model the influence of different levels of P export on decreases in soil P, and
- incorporate into the model the influence of soil properties such as PBI on soil P decreases. A wide range of replicated soils under controlled conditions may be needed for this purpose.

Investigation of the changes in P pools of these field soils as the extractable P concentrations decreased suggested that the majority of the P was not being exported or sorbed, but that Pi was being

converted to P_o , independent of P fertiliser treatment. Most of the soils contained enough P to supply plants in the absence of further P fertiliser applications for periods much greater than the 36 or 48 months of the study. Thus, further work could include:

- further monitoring to provide guidance as to how long these soils can supply the P requirements for optimum pasture production, and
- further monitoring to aid our understanding of the changes in soil P fractions as they are drawn upon.

To assist land managers assess their soil's P supplying potential and risk of P loss, calculation of degree of P sorption saturation (DPSS) using routine Australian extractions was undertaken. Degree of P sorption saturation can be calculated using PSCr measured as per the PBI extraction (P sorbed from an addition of 1000 mg P/kg), and Colwell-P. This means DPSS could be calculated at no, or little, additional cost to the producer or analytical laboratory. The DPSS was relatively low for the extremely low PBI soil, and for other soils with low P sorption capacities, despite their large risk of environmental loss of P. This highlights the need for correlation of DPSS with environmental loss of P from Australian soils, and identification of whether critical DPSS thresholds would change according to soil PBI category. Recommendations for further research include;

- correlating DPSS, calculated using routine Australian extractions, and environmental P loss, across a wide range of sorption capacity soils, and soil P concentrations, and
- assessing whether DPSS can be used as a predictor of a soil's P supplying potential when used in combination with other soil P extractions.

A deep sampling study revealed that a soil with an extremely low P sorption capacity was susceptible to large P losses, with the majority of the applied fertiliser P not recoverable to a depth of 100 cm. These large losses of applied P bring into question whether such soils should be used for agricultural purposes. Even if slow release P fertilisers are used, reaching agronomic optimum soil P concentrations may not be possible for such soils due to their extremely low ability to retain P. However, greater agronomic and smaller environmental soil P concentrations may be possible for these soils if amendments are applied to increase PBI, and ultimately increase the soils ability to retain P. The low P recoveries for the two soils of Chapter 6 question the reliability of the Kjeldahl Pt recovery, when paired with deep soil coring, and suggest improvements in the way P audits are undertaken is required. Thus, it is recommended that:

- the Kjeldahl Pt method, and the P audit approach through soil coring in general, be validated through comparison with more complete P digests, and measurement of actual P loss i.e. in some circumstances through use of lysimeters.

Low P sorbing soils with high organic matter (OM) contents may lose amounts of P of high environmental concern due to OM solubilisation and mineralisation, and release of P of microbial origin.

Indeed, the $\text{CaCl}_2\text{-P}$ concentrations reported in this thesis for the two soils with the lowest PBI were greater than those reported in the literature and suggest that these soils pose a particular risk to the environment.

To date no preferred soil P extraction and threshold has been confirmed to relate agronomic soil P concentrations and environmental risk of P loss for Australian soils. In order for the Australian dairy industry to be sustainable, both economically and environmentally, depletion of excessive soil P concentrations to agronomic optimum should occur. Only once agronomic optimum soil P concentration is reached should the appropriate maintenance P fertiliser program, which accounts for soil sorption and P exported in produce, begin.

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