The assessment and potential for mitigation of phosphorus losses from Organic soils under intensive dairying

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Bernard Simmonds

The development of marginal land under Organic soils for intensive agricultural use is commonplace around the globe, being driven by population growth and the limited availability of alternative, highly productive soils. The development of Organic soils typically involves drainage and the application of lime and phosphorus (P) fertiliser amendments, to rectify acidic soil conditions and poor fertility for pastoral production. However, due to the poor P retention capabilities of Organic soil (a result of low concentrations of P-sorbing metal oxides) there is an elevated risk of P losses in runoff which can have dire agronomic and environmental consequences. The main aims of this thesis were to identify which properties of Organic soils best indicate the potential scale of P losses, the timeframe over which the risk of P losses is greatest, and how soil and land management variables including soil moisture, liming and fertiliser rates, fertiliser solubility, and mineral content can influence the quantities, forms and fractions of P exported from the landscape. A trial was conducted to quantify the importance of a number of soil physical and chemical properties, and land management activities on the potential for P losses. The results of this trial indicated that the effective management of P losses from Organic soils is critical for at least the first 10 years of development, and that P losses were driven by soil P and mineral concentrations. Management within the first 10 years includes drainage, applications of P fertiliser and liming amendments. To this end, a recently-developed acid Organic soil was used in a runoff trial and three lysimeter studies to determine the influence of these variables:

The runoff trial compared the role of soil moisture on the quantities, forms and fractions of P lost in overland and subsurface flow from an Organic soil and a Brown soil. This study demonstrated that soil moisture influenced P loss pathways, but the interactions with soil type (e.g. anion storage capacity) determined the form and quantity of P lost, which may have implications for the drainage or irrigation of Organic soils. The first lysimeter trial determined the influence of liming Organic soils at different fertiliser rates to the forms and fractions of P lost in leachate, retained in the soil and herbage response. The trial found that liming Organic soils had the potential to reduce P concentrations in leachate, and had a positive influence on herbage. The second lysimeter trial determined the importance of P fertiliser solubility for P losses from acid Organic soils at different rates and pH levels. Results showed that the cost of P losses from superphosphate (SSP) treated soils were two to three times greater than reactive phosphate rock (RPR), suggesting that the additional cost of RPR and liming to pH > 5.5 has the potential to offset P losses from SSP fertilisers, making it a more environmentally responsible practice with minimal economic drawbacks. The third lysimeter trial investigated the potential for greater lotus (*Lotus pedunculatus* var. Grasslands Sunrise) to be used in place of white clover (*Trifolium repens*) or ryegrass (*Lolium perenne*) on an acid Organic soil. The trial found no differences in soil P fractions under the three species, and that P uptake into lotus was similar or less than ryegrass and clover, but losses in leachate were commonly greater. Finally, an incubation study was devised to quantify the relative importance of metal oxide concentrations and soil carbon content for P losses, and to determine the potential for the use of mineral amendments to reduce P losses. P losses (as water extractable P; WEP) were reduced by the addition of aluminium sulphate, iron sulphate and calcium sulphate in all cases, and results indicated that P-sorption to aluminium sulphate was the most important factor controlling P release as WEP from these soils.

In conclusion, the findings of this study demonstrated that although Organic soils have the potential to lose far greater quantities of P than other soil types, and this is lost predominantly as subsurface flow, there are a number of management practices and approaches that can alleviate environmental risk and require minimal sacrifices to agronomic productivity. This includes identifying the potential for P losses from Organic and Podzol soils using simple soil tests (Olsen P and P retention or anion storage capacity), accounting for the likelihood of P losses in subsurface and overland flow with regard to soil moisture, irrigation and drainage activities, and mitigating the potential for P losses by increasing lime inputs in combination with sparingly-soluble fertilisers (e.g. RPR).

Keywords: Phosphorus, Organic soil, water quality, liming, fertiliser solubility, soil moisture, soil fertility, hydrophobicity, plant species, lysimeter studies, farm management.

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Abbreviations

Abbreviation	*Definition*
Al	Aluminium
ASC	Anion storage capacity (P retention)
AWHC	Available water holding capacity
BD	Bulk density
C	Carbon
Ca	Calcium
$CaCl_2$-P	Calcium chloride extractable phosphorus
CSA	Critical source area
DMY	Dry matter yield
DPS	Degree of phosphate saturation
Fe	Iron
FRP	Filtered reactive phosphorus (< 0.45 µm)
FUP	Filtered unreactive (organic) phosphorus (< 0.45 µm)
ICP-OES	Inductively coupled plasma-atomic emission spectroscopy
LSD_{05}	Least significant difference ($P < 0.05$)
N	Nitrogen
OM	Organic matter
P	Phosphorus
PP	Particulate phosphorus
RPR	Reactive phosphate rock
SOM	Soil organic matter
SS	Suspended sediments
SSP	Single Superphosphate fertiliser
TFP	Total filtered phosphorus (< 0.45 µm)
TP	Total phosphorus
WDPT	Water drop penetration time
WEP	Water extractable P

Chapter 1

Introduction

1.1 Background

The world's human population has been estimated to increase from 7 billion in 2012 to 8.5 billion by 2025 and have doubled within 60 years (Bolan et al. 2004; Pimentel 2012). Along with anthropogenic encroachment in residential and industrial sectors, there will be a concurrent expansion in agriculture to meet the demands of a growing population. Agriculture currently occupies around 40% of the land surface area (Foley et al. 2005) and at present rates of population growth, agricultural intensification and technical development, agriculture will require the equivalent of 50% of the land surface area by 2030 to sustain current levels of food consumption per capita (Schneider et al. 2011). Globally, grassland-based farming systems have differing degrees of importance and contribute in varying ways to milk production. In Denmark, 63% of the land area is agricultural (OECD 2008) and the area under grass in dairy farms is around 29% with higher proportions for maize and other crops (30% land use). In Ireland, the same land area is given over to agriculture (63%), but grasslands cover 100% of dairy farmed land and stocking rates are twice that of Denmark (2.06 cows ha^{-1}), with around 50% higher milk production (12,300 kg ha^{-1} farmland) (Kristensen et al. 2005). In New Zealand, only 47% of the land area is agricultural (66% grasslands) but is of high importance to the economy, contributing 4% to GDP in 2014, with dairying exports alone representing 25% of all exports (MacLeod and Moller 2006; OECD 2015). Due to the finite nature of quality agricultural land and seemingly boundless growth in the human population, further intensification of existing land (Ehrlich and Holdren 1971; Steinfeld et al. 2006), deforestation and development of new productive land (Lambin and Meyfroidt 2011) and the conversion of marginal land (Ehrlich and Holdren 1971) are predictable outcomes.

Land intensification typically involves increased cropping rates, a shift towards more value-added production, and increased amounts and frequency of inputs (Dumanski and Pieri 2000). Of these attributes, arguably the most significant in terms of both environmental impacts and economic benefits has been the use of fertilisers to increase agricultural production. During the past 40 years, global fertilizer use has increased by around 700%, with a 70% increase in irrigated cropland area (Foley et al. 2005). While the net result of this rapid growth in productivity has been an improved diet for the steadily growing population (Hertel 2011), there is evidence to suggest that staple crops have a biological limit to their maximum yield. For example, Mann (1999) states that the average maize harvest in the United States has increased from 5 metric tonnes per hectare in 1967, to 8 t ha^{-1} in 1997, yet the highest recorded yields have remained at around 20 t ha^{-1} since the mid-1970s. This implies that population growth has the potential to eventually outstrip agricultural production. In conjunction with the current widespread opposition to genetically modified crops (Hertel 2011), an increasing demand for food may necessitate and even improve the economic viability of utilising “marginal” land for agricultural purposes. Intensification of production has occurred recently in New Zealand which has seen an increase in dairy herd size together with fertiliser use. For example, the OECD (2008) report that P fertiliser use has increased 100% in the period 1990-92 to 2002-04. Both changing land use and intensification in New Zealand from the 1980s, especially of dairying, have been linked to a national decline in water quality, including P-enrichment (Ballantine et al. 2010).

1.2 Marginal soils

Marginal land can be defined as land with qualities that at present make it unsuitable for agriculture. Generally, the suitability of land for a particular activity is determined by physical and chemical characteristics of the land and its productivity, including water and wind erosion potential (Larson et al. 1988; Littleboy et al. 1996). Improvements in agricultural technology have increased the productive capacity of marginal soils in many cases. For example, soils with low natural P concentrations and high organic matter content (i.e. the Waituna Lagoon catchment, Southland, New Zealand) can require significant additions of P fertiliser to improve production. However, there are difficulties centred around the development of marginal lands with a strong reliance on fertilisers. For example, the inherently high nutrient loss characteristics of some marginal soil types (e.g. Organic soils) can render conventional farming practices inefficient (Iho and Laukkanen 2012) and result in detrimental environmental effects including the eutrophication of freshwater systems (Mann 1999). Because of this, the conversion of marginal land to meet the demands of population growth is considered less desirable than further intensification of existing agricultural land (Cassman et al. 2002).

1.3 Phosphorus in the environment

Phosphorus (P) is frequently the main limiting nutrient for plant growth in terrestrial and aquatic ecosystems (e.g. McDowell et al. 2009). While there are obvious economic advantages to enhancing soil fertility by adding fertilisers, including increased animal stocking rates and production (MacLeod and Moller 2006), P is the most expensive macro-nutrient applied to pastoral soil (Edmeades et al. 2006; Gilbert 2009). Additionally, anthropogenic P inputs are a causative agent of accelerated aquatic eutrophication and can increase rates of eutrophication beyond natural levels (Abell et al. 2010; Qin 2009). Eutrophication is defined as the nutrient enrichment of aquatic ecosystems and frequently results in an array of symptomatic changes that impair water use (Likens et al. 1971). The process of eutrophication often occurs in sequential steps. Nutrients are primarily introduced from terrestrial landscapes by pathways that include infiltration- and saturation-excess overland flow (McDowell et al. 2004). Nutrient enrichment is followed by a period of increased primary productivity and succession in algal communities that typically culminates with the dominance of cyanobacterial species or extensive periphyton growth (Carpenter et al. 1998a; Khan and Ansari 2005). Long periods of phytoplankton growth can exhaust dissolved inorganic nutrient concentrations in the epilimnion, with senescence transporting organic nutrients to the hypolimnion, stimulating enhanced microbial decomposition which leads to hypolimnetic anoxia and the regeneration of ammonium (Borowiak et al. 2010; Meersche et al. 2004). Phosphorus in the water column is then able to become aggregated into insoluble flocculent and particulate organic forms which settle out and continue to bind P at the sediment/water interface. These aggregates dissolve under anoxic conditions, allowing filterable reactive phosphorus (FRP) to diffuse into the hypolimnion, further perpetuating eutrophic symptoms by creating a positive feedback loop that can be extremely difficult to mitigate once established (Bennion et al. 1996; Johannessen and Dahl 1996; Kalff 2002a). Other attributes of a eutrophic water body include the loss of biodiversity as eutrophic conditions favour competitive exotic species (Codd 2000), predatory dinoflagellate genera (e.g. Pfiesteria) (Burkholder and Glasgow 1997), reductions in water transparency, undesirable odours, and the unsuitability of water for stock or human consumption (van den Brandt and Smit 1998). Bennett et al. (2001) determined that global inputs of P to terrestrial soils and freshwater ecosystems ranges from 33.5 and 38.5 Tg (1 Tg = 1 million metric tonnes) annually. The global cost of accelerated eutrophication is difficult to quantify; having negative impacts on not only recreational activities, but also commercial ventures, including tourism and food. For the United States alone, eutrophication accounts for 60% of impaired river reaches (Smith 2003), while the annual cost of water pollution control is estimated at US $80 x 10^9 per year (Carpenter et al. 1998b). In New Zealand, between 73% and 63% of freshwater lotic systems are P limited, and 14% and 20% are N and P co-limited (North and South Islands, respectively) (McDowell, Larned and Houlbrooke 2009).

Driven by the declining quality of fresh water resources (Abell et al. 2010; Scanlon et al. 2007), a considerable amount of research has been conducted with the intent to maximise production and minimise P export from the landscape. Strategies include; reducing mobile P fractions through the use of slow-release fertilisers, such as RPR or serpentine super (McDowell and Catto 2005); trialling soil additions that reduce phosphorus flux, for example, alum ($Al_2(SO_4)_3{\cdot}14H_2O$) (Moore and Miller 1994); and timing fertiliser applications to prevent losses to overland flow (McDowell and Catto 2005).

1.4 Phosphorus in soils

Phosphorus in soils naturally originates from the weathering of P-bearing minerals in rock substrata (Föllmi et al. 2009). As soils weather, the proportion primary mineral P (e.g. apatite) to labile inorganic and organic P fractions change; termed pedogenesis (Walker and Syers 1976). The total P content of the soil at a given time is a combination of organic and inorganic mineral components, all with varying degrees of solubility and abilities to supply plant available P (McDowell et al. 2001). Phosphorus deficiencies in agricultural soils are mitigated by the application of fertilisers. Fertilisers range in P composition and plant availability, and are applied with regard to the physiochemical attributes of the soil, the specific requirements of the crops, environmental factors (e.g. precipitation) and cost-effectiveness.

Organic and inorganic soil P fractions – Around 30 to 80% of the total P present in soils exists as an organic fraction derived from the decomposition of plant, animal and microbial cells (Harrison 1987). New Zealand has a high number of soils with organic P fractions frequently in excess of 60% of total P (Cornforth 1998). Orthophosphate monoesters and diesters comprise some 60-90% of the total organic-P fraction and can form insoluble mineral compounds with iron, calcium and aluminium ions (Chang and Jackson 1957). There is debate over the plant and algal availability of organic P, with studies showing high and low availability depending on the exact form of organic P present in the soil and soil solution (Turner et al. 2003).

Depending on the composition of the organic matter (OM), negatively charged carboxyl/hydroxyl function groups of OM can compete in solution with orthophosphoric acid esters to form bridging ligands with positively charged minerals, including iron (Fe) and aluminium (Al) oxides (Gu et al. 1994; Hinsinger 2001). These sorption processes subsequently influence the amount of P in active and fixed pools. Inorganic forms of P include apatite, complexes of calcium (Ca), Fe and Al phosphate, and adsorbed phosphate (Chang and Jackson 1957). The importance of these P precipitates and sorption products to P availability relates to their relative quantities within the soil, the presence of competing P-fixing materials, and the physicochemical properties of the soil (e.g. pH, moisture regime and redox potential).

Organic and inorganic aqueous P fractions – Forms of P lost in runoff from agricultural land have been operationally defined: first, physically by filtration at 0.45 µm and secondly, chemically by whether or not the fraction of P is detectable (or reactive) with the commonly used acid-Mo based colorimetric technique of Murphy and Riley (1962) and subsequent colorimetric variants (e.g. Watanabe and Olsen 1965). The fraction that is reactive and < 0.45 µm is called dissolved or soluble reactive P (DRP or SRP), but more correctly called filtered reactive P (FRP). The digestion (e.g. persulphate; Eisenreich et al. 1975) of a sample which passes through the filter enables the determination of total filtered P (TFP). The difference between TFP and FRP is unreactive (FUP) P which is commonly thought to contain mostly organic P species, but can also contain some inorganic P species such as polyphosphate which are colorimetrically unreactive (McDowell et al. 2001). Phosphorus that is greater than 0.45 µm is termed particulate P (PP) and can contain inorganic and organic P species. The proportion of PP in a sample is determined by difference of total P determined on a digested unfiltered sample and TFP.

These operationally defined P fractions have important implications for freshwater eutrophication. For example, FRP is highly bioavailable to periphyton and hence is the controlling factor in lotic systems (flowing streams and rivers) where there is limited residence time or opportunity to uptake P. In lentic systems (lakes, reservoirs and estuaries) both filtered and particulate fractions play a significant role as external P inputs are coupled with internal P loading, stimulating algal growth over long periods of time due to annual cyclic mixing and stratification events (Bennion et al. 1996; Kalff 2002b). There is debate over the plant and algal availability of organic P, with studies showing high and low bioavailability depending on the exact form of organic P present (Turner et al. 2003). Despite being more important in lotic systems, PP can be filtered from the water by periphyton or macrophytes (e.g. in a wetland) resulting in flow attenuation and an increase in the advective transport of FRP from the sediment (Dodds 2003). Although wetlands act as an important filter for PP (Cooke et al. 1992), they can act as a source of P when loading rates exceed the long-term sink capacity, and more importantly, when anerobic conditions occur leading to the dissolution of FRP (Richardson 1989; Richardson et al. 1996). The eutrophication symptoms exhibited by lagoons and estuaries represents a convergence of lentic and lotic systems in that high concentrations of FRP will stimulate immediate algal productivity, as with lentic and lotic systems (Anderson et al. 2002), and that deposition of PP can become a major component of algal growth, as with lotic systems.

1.5 Catchment attributes that affect P transport

Catchments can be highly diverse in terms of their soils, topography, hydrologic regimes and land use and management characteristics. As a result of these differences, the pathways for P losses from terrestrial landscapes are also spatially variable. Small areas within catchments that have disproportionately high P loss characteristics are termed critical source areas (CSAs) (McDowell et al. 2004) and generally occur where transport mechanisms (e.g. overland flow) and contaminant sources (e.g. stock tracks) overlap (McDowell and Srinivasan 2009).

1.5.1 Land use – Agricultural soils have a higher potential for P loss as they receive additional phosphorus in the form of fertilisers or dung and are prone to treading, compaction or erosion exacerbated by animals and machinery (Figure 1.1). Compaction and treading can exacerbate erosion and overland flow by decreasing the macropore content of a soil and increasing its bulk density, influencing the movement of water through the soil (Nguyen et al. 1998). This can be a major concern in southern New Zealand, where animals are placed in fields with a forage crop (e.g. Brassica rutabaga L.) during winter. The higher soil moisture content at this time results in enhanced rates of physical degradation and runoff as moist soils are structurally less resistant to treading (McDowell et al. 2003a; McDowell et al. 2003b). The type and density of stock also play a key role. McDowell and Wilcock (2008) compared the relative losses of nitrogen, P and suspended sediment (SS) from New Zealand catchments containing exotic plantation and native forest (vegetation), sheep, deer, dairy and multiple stock types (mixed). The authors found that mean P losses were not significantly different between deer, mixed and dairy land uses, but were higher than sheep and vegetation. This indicates that some stock types are potentially associated with greater rates of P loss per unit area. These findings could be explained by the greater weight of cattle enhancing treading and compaction (Drewry et al. 2000), and the behavioural attributes of deer, including wallowing and fence line pacing (McDowell et al. 2006). The crushing of plant material can also increase P losses in subsurface flow (McDowell et al. 2003b), as indicated by Sharpley and Smith (1989) who recorded losses as high as 40% when plant residues were incorporated into soils. While some management activities clearly influence the quantity of P exported from a landscape, the availability of FRP for export from soils is predominantly a function of soil mineral content and pH, moisture regime, oxygen-reduction processes.

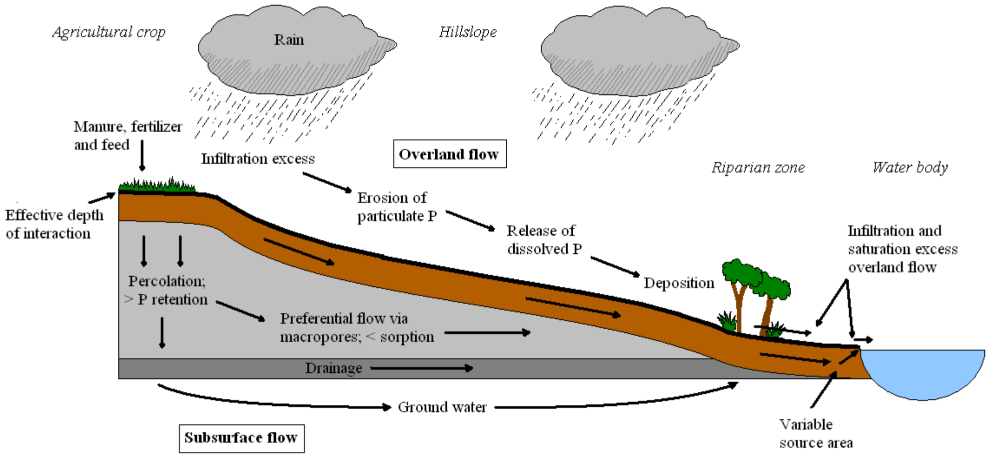

Figure 1.1. Conceptual diagram of catchment P transport processes (adapted from Johnes and Hodgkinson 1998; McDowell et al. 2004).

1.5.2 Soil pH – Soil pH influences the availability of P by controlling levels of metal oxides that can precipitate with P, including Al, magnesium (Mn), Fe and Ca. Soluble calcium phosphate precipitates in alkaline soils at pH values of around 8 (Ferguson et al. 1973; Richardson et al. 1996) and may eventually be converted to sparingly soluble tricalcium phosphate and then to new apatite minerals (Chang and Jackson 1957). The dissolution of Ca phosphates occurs under acidic conditions where Al and Fe phosphates are able to precipitate (pH $\leq$ 3.5 and pH 4-6, respectively) (McDowell et al. 2001; Oburger et al. 2011). However, under acidic conditions, Al concentrations can build to phytotoxic levels and inhibit the P uptake capacity of plants (Haynes 1982), further limiting P availability as Fe and Al phosphates are also insoluble and not plant available.

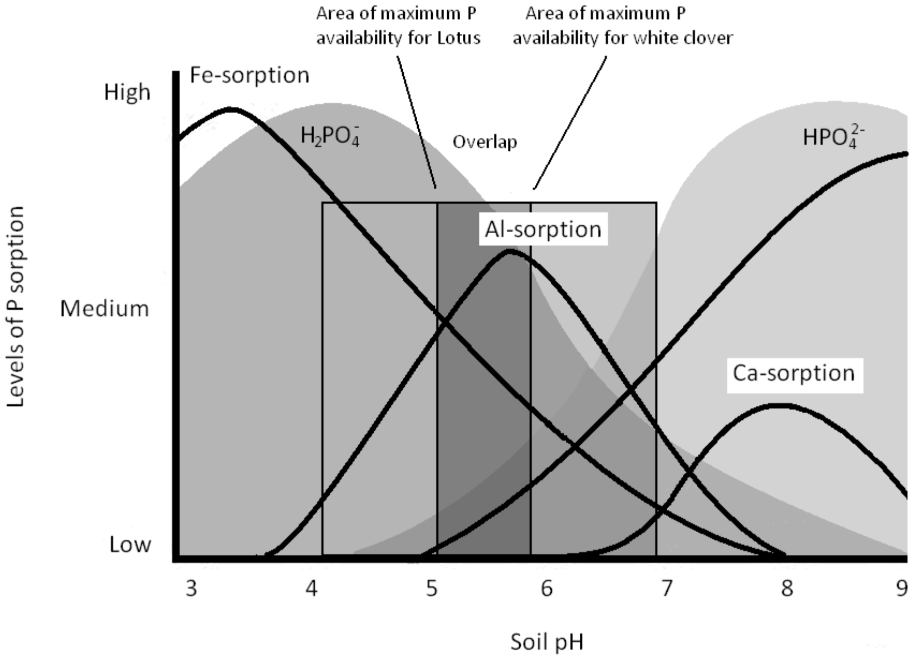

Figure 1.2. The sorption and solubility of phosphate species and overlapping availability to white clover and *Lotus* sp. with pH (adapted from Lindsay 1979).

1.5.3 Moisture regime – Wetting and drying cycles in acidic wetlands are coupled with alternating anaerobic and aerobic soil conditions due to the reductive effects of microbial activity during inundation, and oxygenation following drying. When soil conditions become anoxic, ferrous iron is used as a supplementary terminal electron receptor in lieu of oxygen, and Fe (III) phosphates are reduced to Fe (II) phosphates, promoting the release of P previously occluded by the iron compounds (Mack and Barber 1960). Subsequent drying processes further exacerbate P release as soil microbes become mineralised during dry periods, and then liberate mineralised inorganic P to the overlying water column when re-wetted (Olila et al. 1997).

1.6 Transport processes

The quantity and to some degree the form of P lost from land to water can be determined by the transport pathway. Runoff is a combination of surface flow and subsurface drainage (also called leaching), by which all forms of P are transported (Figure. 1.1). Atmospheric deposition of P tends to be minor (McDowell et al. 2009).

1.6.1 Overland flow – The two major processes of surface runoff are saturation excess (Dunne) and infiltration excess (Hortonian) overland flow (Table 1.1, Figure 1.1). Saturation excess overland flow occurs in soils that have met their capacity for moisture storage (Dunne and Black 1970) and a precipitation rate that is less than or equal to the saturated hydraulic conductivity of the land surface causes water exfiltration at the surface (Kollet and Maxwell 2006). Infiltration-excess runoff occurs when the rainfall rate exceeds the saturated hydraulic conductivity of the land, resulting in an accumulation of water (ponding) at the surface as the soil drainage takes place (Kollet and Maxwell 2006). Due to the large amount of kinetic energy associated with surface runoff, especially infiltration-excess surface runoff, erosion occurs and PP is preferentially lost over filtered forms (Kleinman et al. 2009). However, there is some evidence to show that in grassland (and grazed pastoral) situations, the filtration action of the pasture, and low rainfall intensities generally associated with climates where pasture is grazed, causes filtered P to be preferentially lost over PP (Nash et al. 2000).

Phosphorus fertiliser losses in overland flow arise from a number of incidental and systematic effects (Dougherty et al. 2011) including the timing and type of fertiliser used with regard to precipitation (McDowell et al. 2010), the physicochemical properties of the soil, including its anion storage capacity (Morton et al. 2003) and pH (McDowell et al. 2002), and soil P concentrations (McDowell and Sharpley 2001a). However, agricultural landscapes with a long history of intensive management can still contribute significant P loads to aquatic waterways in spite of reductions in fertiliser inputs. This takes place where mineral soils and sediments accrue P over time, eventually becoming ‘over fertilised’ (Haygarth et al. 1998). These soils can have internal P supplies that exceed external inputs (Dunne et al. 2010) and phosphorus losses occur as FRP is diffused or advected from underlying soil pore waters to overland flows (Moore et al. 1998).

Table 1.1. Inputs and pathways with associated P fractions (adapted from Johnes and Hodgkinson 1998).

Fractions	Fertiliser	Manure	Soil particles	Leaching	Eluviation	Subsurface flow in drainage	Overland flow	Soil through flow	Selective transport of fines	Retention, cycling and export
Particulate Inorganic P	-	-	✓	✓	✓	✓	✓	✓	✓	-
Particulate Organic P	-	✓	✓	-	-	-	✓	-	-	✓
Filtered Reactive P	✓	-	-	✓	✓	✓	✓	✓	-	✓
Filtered Unreactive P	-	✓	✓	-	-	✓	-	-	✓	✓

1.6.2 Subsurface flow – In comparison to overland flows, subsurface flow (also called leaching) is a relatively slow mechanism for sediment and P dispersal (McDowell et al. 2003b). Phosphorus transport in subsurface flow is more difficult to monitor than surface flow, and until relatively recently was considered insignificant in the context of overall catchment P losses (Brookes et al. 1997). However, the concentration of P in subsurface flow can be greater than in surface runoff due to extended periods of contact with soil (McDowell and Condron 2004), and exceed the threshold required to stimulate symptoms of eutrophication (McDowell and Sharpley 2001a) making it an important consideration for P management. The subsurface transport of P tends to occur as a result of low intensity rainfall events where moisture is more readily conducted within the soil matrix, as opposed to high intensity rainfall that leads to overland (Hortonian) flow (McDowell 2012b).

There are two ways that P can be lost via subsurface flow, namely matrix flow and bypass (preferential) flow (Table 1.1). Matrix flow refers to slow flow that occurs through the bulk soil, whereas preferential flow is a transport pathway that allows large amounts of water to flow through a relatively small area of the soil (Simard et al. 2000). The concentration of P lost will depend on the release characteristics of the soil matrix. To some extent the concentration is also dependent upon the P sorption/desorption characteristics of the macropore walls, but more often the walls will not interact with the water flowing by, hence the term preferential or bypass flow (Sinaj et al. 2002). Examples of preferential flow pathways are cracks, root holes and worm holes. Preferential flow paths have been shown to transport P under high flow events. Stamm et al. (1998) measured P export from an intensively managed grassland catchment, and found P was transported in both filtered-reactive and particulate P forms, with 227 g FRP ha^{-1} lost from a single site within 2.5 months. When coupled with artificial drainage systems, water and entrained P can be quickly transported to drainage networks. Deep drainage to groundwater can occur, but is usually considered of negligible impact on surface water bodies as the P is usually sorbed and retained before groundwater escapes into streams as baseflow. However, if the soil has low capacity to store P and groundwaters are anaerobic, facilitating P to be soluble, then groundwater could be an important source of P into freshwaters (McDowell et al. 2004).

1.7 Phosphorus loss from Organic soils

Organic soils are estimated to cover a global land area of between 230 and 450 million hectares (Armentano 1980), around 200,000 ha of which are in New Zealand (Gibbs 1980). The majority of New Zealand's Organic soils occur under pasture, in wetlands, or under forest-produced acid litter in areas of high precipitation (Hewitt 2010). Many of these have been drained to improve aeration and resistance to physical damage from machinery and stock (O'Connor et al. 2001). However, drainage accelerates rates of erosion (Marttila and Kløve 2010a), peat mineralisation (O'Connor et al. 2001) and the desorption of P from previously reductive soils (Lovley and Phillips 1986; Stepniewska et al. 2006). Following drainage and development, Organic soils will typically have an exceptionally poor nutrient capacity (Zak et al. 2004) in addition to low pH levels. Other characteristics of Organic soils include low bulk densities, high cation (e.g. Ca^{2+}) exchange and low anion (e.g. $H_2PO_4^-$) storage capacities, high C/N ratios, low load-bearing strength, poor thermal conductivity, high shrinkage potential and high total water capacity with only moderate plant-available water (Hewitt 2010; Robson et al. 2011). Of the 200,000 ha found in New Zealand, around 146,000 ha has been converted into intensive land uses such as dairying (Ausseil et al. 2015). However, there are several factors that indicate that, during and after development, P losses may be exceptionally high under intensive dairying.

The processes of FRP flux are enhanced in soils with high porosity and hydraulic conductivity values, such as Organic and Podzol soils. This is due to the combination of high surface areas within the soil matrix for P flux to occur across and the relative ease at which the soil solution is able to move within the matrix and leach to groundwater (Stutter et al. 2005). A fluctuating groundwater level, a common accompaniment to Organic soils due to their low lying position in many catchments (Guérin et al. 2011), also more readily saturates topsoil where P is most enriched leading to enhanced losses by drainage and cyclic wetting and rewetting processes (Butterly et al. 2009; Meissner et al. 2008; Rupp et al. 2004). However, the main factor influencing the availability of P loss in Organic soils is a low P retention, otherwise known as anion storage capacity (McDowell and Condron 2004). The anion storage capacity (ASC; also referred to as P retention) describes the soil's capability to retain nutrients (O'Connor et al. 2001). Organic soils typically have a low ASC, due to little mineral soil which would contain P-sorbing Al- and Fe-oxides (Zak et al. 2004; Robson et al. 2011). The quantities of these materials ultimately influence the P retention and bioavailability properties of the soil. For example, aluminium-oxides have a high sorption affinity for P and studies have found that the injection of Al-based precipitation chemicals can radically increase the retention capacity of wetlands (Ronkanen and Kløve 2009). In eutrophic wetlands the precipitation of Fe (III) oxyhydroxides determines P export from soils by retaining P via precipitation under aerobic conditions (Rupp et al. 2004), and the desorption of P when Fe (III) reduces to Fe (II) under anoxic conditions (Lovley and Phillips 1986). Calcium precipitates can also control the concentration of P in soil solution via a sequence of solubility products. Initially P is adsorbed onto calcite, then subsequent steps convert this into precipitates of monocalcium, dicalcium, octocalcium and finally hydroxyapatite; a highly stable compound (Frossard et al. 1995).

The low ASC values and enhanced FRP flux and variable soil moisture associated with Organic soils contribute significantly to their definition as 'marginal' soil types. High pasture production on Organic soils therefore requires additional development beyond that of high quality soils.

This includes applications of lime (or similar) to optimise pH levels for crops and intensive fertilisation to account for poor nutrient retention qualities. Nevertheless, high pasture production on Organic soils has commonly been achieved with P fertiliser application rates beyond that of higher quality soils. For example, the Olsen P target ranges to sustain 97% of maximum pasture production are 35–45 mg P L^{-1} for peat soils and 20–30 mg P L^{-1} for ash soils (Roberts and Morton 1999). The rate at which ASC changes on Organic soils and how this is influenced by land management (e.g. cultivation frequency) is unknown, but clearly will affect P losses.

1.8 Organic soil drainage and development

Organic soils are associated with a variable moisture regime, which plays an important role in the availability of P. Under moisture-rich conditions, flux rates of FRP can become enhanced leading to high concentrations of dissolved P in the soil root zone that may be subsequently lost by lateral transport and leaching processes (de Mars and Wassen 1999; Stepniewska et al. 2006). Furthermore, under very dry conditions, water repellence; or hydrophobicity can also be extremely high in Organic soils. Research by Sharp et al. (2006) described hydrophobic organic material as having a greater coagulation potential than hydrophilic OM, due to possessing a significantly higher charge density. The coagulation process is optimised under acidic conditions and involves charge neutralisation, complexation and precipitation, and ligand exchange mechanisms (Sharp et al. 2006). Therefore, soil hydrophobicity could be a particularly important aspect of acidic wetlands with limited solution P penetration as a result. Deurer et al. (2011) compared hydrophobicity in 50 grassland sites spanning the 10 most dominant New Zealand soil orders. Organic and Podzol soils were found to exhibit the highest degree and persistence of water repellency, due to the hydrophobic nature of organic matter itself and the low quantity of exposed hydrophilic matter in the soil. Seasonal soil drying also causes hydrophobicity in 70% of New Zealand top soils (Deurer and Müller 2010) which indicates that soil moisture status could exacerbate overland flows and the transport of nutrients following precipitation; particularly following manure applications that supply both additional organic matter and readily soluble nutrients (McDowell 2012a). This is of particular concern as it means that runoff will transport P during summer when the potential for water quality impairment is greatest. There is also evidence to indicate that increased infiltration-excess surface runoff (as opposed to drainage or saturation-excess surface runoff) has more energy and results in the erosion of particulate P, which as noted above will degrade water quality in lakes, impoundments or lagoons (Kleinman et al. 2009). Although the processes involved in P loss to drainage, due to anaerobic conditions, are known, little is known of the potential P losses (and fractions therein) in surface runoff of Organic soils of different antecedent moisture.

1.9 Management activities influencing P losses from Organic soils

Typically, P is lost from soils from one of four sources - 1) the soil, 2) fertiliser, 3) dung (or effluent) and 4) the plant itself (McDowell et al. 2007). The relative proportion of each source varies. Many strategies exist to mitigate P loss from the various components of an intensive dairy farm, but have not been fully tested on Organic soils.

1.9.1 Rate of P application – Multiple smaller P fertiliser applications are commonly undertaken, particularly where soils with high P-sorption properties (e.g. calcareous soils) are concerned (Burkitt et al. 2010a). However, there is little evidence to suggest that higher dry matter yields will result when soil test P concentrations are above the agronomic optimum. Instead, many studies have noted accelerated rates of P loss under multiple P application regimes. For example, Burkitt et al. (2010b) contrasted the P runoff risk following single and split phosphorus fertiliser applications on a soil. The authors found that three applications of 13.3 kg P ha^{-1} resulting in higher overall dissolved and total P loss than a single 40 kg P ha^{-1} application, supporting a single application during periods when surface runoff events were unlikely (i.e. summer). High rates of smaller super-P applications result in higher overall total P (TP) loss due to an increased risk of coinciding rainfall events (in comparison with a single, large super-P application), but high water solubility of the fertiliser orthophosphate is the primary cause of this. Multiple small applications of low-solubility RPR could result in higher soil P availability and relatively lower TP losses when fertilising coincides with rainfall.

1.9.2 Liming – Phosphorus availability in mineral soils with < 5% organic matter (OM) is greatest at a pH of around 6.0 – 7.0, while in soils of higher organic content P availability is greatest at a pH range of 5.0 – 6.0 (Wolf 1999). The ionic form of inorganic P changes with pH (Figure 1.2), but more importantly tends to be associated with Al and Fe under acidic conditions and Ca under alkaline conditions. Under very acidic conditions (pH < 4.0), Al concentrations can build to phytotoxic levels and also inhibit the P uptake capacity of plants (Haynes 1982). This is generally mitigated by the application of lime (or in some cases, gypsum) to increase pH for optimal nutrient availability (Murphy and Stevens 2010). The application of lime can increase the mineralisation of OM, causing P housed within OM to be released, and also increase the solubility of P associated with minerals that precipitate at more acidic conditions (Fe-P). It is unknown if this would result in losses as inorganic or organic P forms from Organic soil, or whether (due to a low ASC), this P is likely to be lost.

1.9.3 Low solubility P fertilisers – The risk of surface runoff of P is greatest when highly soluble forms of P fertiliser (e.g. SSP) are applied when a runoff event is likely. In areas of high precipitation, the risk of incidental P loss can be reduced by using low-solubility forms of P fertiliser. Reactive phosphate rock has very little water soluble P, but contains as much or greater total P concentration to SSP. Due to its low solubility, the slowly releasing RPR can take several years post-application before soil test P targets are met. For example, McDowell et al. (2010) tested the relative P loads in streams from two 12 ha catchments, each fertilised with RPR for 3 consecutive years, and SSP for 2 years. The authors noted FRP and TP loads were 58% and 38% lower in stream flow when RPR was applied, instead of SSP. Agronomically, Sinclair et al. (1993) showed that after applying RPR for 3 years it has the same pasture production as SSP in areas where rainfall > 800 mm and soil pH was < 6.0. However, RPR is still a viable fertiliser from an agronomic perspective because it can eventually provide the same potential dry matter yield (per application size) as SSP (McDowell and Catto 2005). This raises the question of whether poorly-soluble fertilisers can be used in place of conventional SSP on Organic soils, where two factors could negate the potential environmental benefit of RPR compared to SSP. The first is that because RPR contains apatite which increases in solubility in low pH environments, the lower pH of Organic soils (even after sustained liming) could increase the dissolution rate of RPR. The second is that it is likely that due to high hydraulic conductivities, that subsurface flow is the dominant pathway of P loss meaning that flow will have longer to interact and be adsorbed (even if only to a small degree) by the soil matrix. In extreme cases, RPR applications on acidic Organic soils could result in an increase in solubility of RPR, leading to enhanced P loss rates to such an extent that SSP would be as effective as RPR.

1.9.4 Vegetation types – Legumes like greater lotus (*Lotus pedunculatus*) are beneficial in agriculture because they are able to fix nitrogen (N), reducing N fertiliser requirements. Additionally, some legumes favour low pH soils (approximately 4.7), are shallow rooting and assimilate P quickly (Sheath 1981). This potentially makes them suitable for soils where P retention and plant growth is a concern, for example acidic Organic soils. When plants are grown under P-limited conditions, plant roots secrete organic acids and acid phosphatase enzymes which enhance the dissolution of organic phosphorus (Tadano et al. 1993). For example, White lupin (*Lupinus albus*) grown under P deficiency secretes a significant amount of acid phosphatase (Miller et al. 2001). New Zealand Organic soils have a high content of organic P, so the use of acid phosphatase-secreting plants has good potential for maximising forage crop yield with relatively minor P fertiliser inputs. Additionally, *Lotus corniculatus* has been found to produce significantly less methane in sheep (mean = 11.5 g kg^{-1} dry matter intake; DMI) in comparison to pasture (mean = 25.7 g kg^{-1} DMI) and lucerne (mean = 20.6 g kg^{-1} DMI) (Waghorn et al. 2002). A major advantage to legume forage crops is the reduced risk of bloat due to high condensed tannin content. Bloat is caused when a stable froth of soluble plant proteins and cellular organelle particles from leaf mesophyll combines with the slime produced by ruminant bacteria (Howarth et al. 1991). Condensed tannins reduce bloat by causing plant protein to precipitate or come out of solution, thereby inhibiting bacterial activity (Majak et al. 2003). Legumes are common on acid soils and is successfully used as a winter forage crop in European and Mediterranean agriculture (Mihailović et al. 2008), and have proven good survival rates in cold temperate climates (Wills et al. 2003). However, there are difficulties associated with some legumes (e.g. lotus) in that they require a long period of establishment and, in soils of higher fertility, competitive exclusion by other vegetation can limit their potential use as a pastoral vegetation (Lowther et al. 2012). Lotus dry matter production and plant density declines with time under dairying, but this could be slowed using infrequent grazing, which also slows the ingression of weeds (Minneé et al. 2007). Research undertaken on a well-drained, fertile sandy loam soil has shown that in monocultures, legumes have potential to increase milk solid production in comparison with mixed swards (McDowell et a. 2014). However it is unclear if the same is true for Organic soils, where the higher tolerance of lotus to low pH and limited nutrients could yield a productive advantage over more commonly opted legume and grass pasture species (e.g. white clover and ryegrass).

1.9.5 Soil amendments – The poor P retention characteristics of soils with low quantities of iron and aluminium can be mitigated through the addition of soil treatments. Soil treatments can improve the retention of phosphorus by increasing the number of P sorbtion sites, thereby decreasing its mobility. The supplementation of soils with aluminium sulfate (alum) is one such example. In acid ($pH < 5$) Organic soils, free Al in solution can bind with organic matter (OM) to form OM-Al complexes with which inorganic P can form metal ligands (Darke and Walbridge 2000). This effectively reduces the export of PO_4^{3-} from the catchment system. McDowell (2010) trialled the effectiveness of 20 kg ha^{-1} alum to reduce P losses from a high-rainfall environment. The results did not successfully prove alum was able to decrease P losses and it was speculated that the alum was easily removed by precipitation. However at high concentrations (around 4.5 kg Al m^2) trialled by Smith et al. (2001), alum reduced soluble reactive P in runoff from swine manure-treated fields by 84%. As the solubility of OM-Al-P complexes increase significantly at pH levels above 5.4 (Darke and Walbridge 2000) and as Al is phytotoxic at high concentrations; stunting plant root systems and greatly limiting growth (Hocking 2001), alum is unsuitable for use on high pH soils. These studies suggest alum has the potential to reduce the non-point source export of P on soils of low pH in areas of low precipitation. Other soil treatments or amendments include bauxite residue; a by-product of refining bauxite into alumina (McDowell and Nash 2011). Application rates of 10-20 t ha^{-1} have been shown to provide effective retention of P for up to 5 years (Summers et al. 1996), while at higher rates (270 t ha^{-1}) in combination with waste gypsum (to alleviate the high pH), bauxite residue has been found to decrease P loss by up to 98% (Vlahos et al. 1989). However, at these concentrations bauxite residue is potentially toxic or disruptive to the rumen pH of cattle, and there are transport and supply issues (McDowell and Nash 2011).

1.10 Objective, hypotheses and thesis outline

It is clear from the preceding literature review that the intensification of Organic soils is linked to potentially costly environmental and economic implications. There is a clear need to effectively manage agriculture on these soils if the future demands of a growing population are to be sustainably met without damaging natural ecosystems beyond current levels.

The aim of this thesis is to define the key limitations of the intensification of Organic soils in order to define management practices that are lucrative from an agronomic perspective, yet are environmentally responsible. The overall hypothesis is that P loss from Organic soils and potential water quality impacts are high immediately following development, but can be decreased by changes in soil properties and better management. Farm management areas that can contribute to P transport from Organic soils have been identified from the literature, and the following six key project objectives have been defined:

1: Determine soil and management practices that influence the loss of P from soils over time.
2: Determine the relative potential and form of P loss under low-intensity rainfall for Organic soils as a function of Olsen P and moisture regime (specifically low moisture and hydrophobicity).
3: Determine the bioavailability and quantity of P lost with increasing pH in Organic soils.
4: Determine losses of P from Organic soil treated with RPR and super-P at different pH levels.
5: Determine the relative importance of Al, Fe, Ca and C for Organic soil P losses.
6: Determine productivity and losses from an Organic soil with lotus, ryegrass or clover in monoculture.

Chapter 2

Potential phosphorus losses from Organic and Podzol soils: prediction and the influence of soil physico-chemical properties and management

2.1 Introduction

The transfer of P from soil to water is a process that occurs in natural ecosystems. However, converting land to agriculture results in substantial changes in the physical, chemical and biological properties of soils, which together with an increase in the quantity of P in soil can increase the risk of P loss from soil to water bodies (McDowell et al. 2001; Haygarth and Condron 2004; Haygarth et al. 2013). For instance, tillage aerates topsoils accelerating the mineralisation of OM and increasing the availability of organic P compounds (Kasimir-Klemedtsson et al. 1997; Horne and Sojika 2002; Rastogi et al. 2002). However, tillage also increases drainage and potentially P loss especially if subsurface runoff is intercepted by artificial drainage (Schelde et al. 2006; Kleinman et al. 2011). In contrast, drainage may also increase the ASC of peat soils (O’Connor et al. 2001), presumably as the soil decreases in C content and becomes more “mineral like” under oxic conditions. This could therefore decrease the potential for P loss (McDowell and Condron 2004).

Organic and Podzol soils occur in similar lowland swampy areas; podzols form under acidic forest litter and high rainfall, while Organic soils form where there is poor drainage leading to an accumulation of organic matter. Increasingly they are being developed for intensive agriculture (e.g. dairying) as the competition and price of more suitable land increases (Ehrlich and Holdren 1971; Asner et al. 2004). To maintain high pasture production, these soils are drained and considerable quantities of lime and fertiliser are applied to correct acidic soil pH and poor fertility (O'Connor et al. 2001). However, concentrations of Al and Fe tend to be low in the surface horizons resulting in poor sorption of added P (e.g. Lundström et al. 2000; Riise et al. 2000; Pokrovsky et al. 2005). In order to maximise production, it is recommended that Olsen P is maintained at greater concentrations in Podzol and Organic soils than in most other soils. For example, in New Zealand the target Olsen P concentration to sustain 97% of maximum pasture production is between 35 and 45 mg P L^{-1} for peat (i.e. Organic) Soils and between 20 to 30 mg P L^{-1} for ash and sedimentary soils (Roberts and Morton 1999). Relatively little is known of the potential for soils classified as Organic and Podzol soils in New Zealand to lose P. However, as P loss from soil to water is related to Olsen P concentration (McDowell and Condron 2004), maintaining an agronomic optimum Olsen P for Organic soils may result in greater P loss.

The main objective of this study was to estimate the potential for P loss in surface and sub-surface runoff with water and dilute $CaCl_2$ extractable P concentrations determined in a range of Organic and Podzol soils. These extracts have been shown to be good estimators of P loss by McDowell and Sharpley (2001) and McDowell and Condron (2004), but their dataset contained few Organic or Podzol soils. A secondary objective was to predict water and dilute $CaCl_2$ extractable P from more common soil physical and chemical characteristics (e.g. Olsen P), and how these change with time (e.g. since conversion from native landuse). This would enable estimations of P losses to be made where these variables are already known.

2.2 Materials and Methods

Soils were collected from the Waituna catchment, a predominantly dairying-oriented coastal catchment in Southland, New Zealand (Figure 2.1). The catchment receives approximately 1,200 mm annual rainfall (Risk 2011). The soils are poorly-drained and were classified as per New Zealand soil taxonomy as Acid Fibric Organic (Invercargill and Otanomomo) and Perch-Gley Podzol (Kapuka, Tisbury and Tiwai) soils (Hewitt 2010). Using soil maps, approximately 40 sites were chosen of each soil Order for a total of 80 paddocks plus six additional “reference sites” consisting of undeveloped soils that were still in scrub (three of each Order).

A questionnaire detailing the development and management histories of each paddock was completed with land owners. Data from the questionnaire was used to explain variation in each paddock’s soil physical and chemical data. The questionnaire obtained data on: the time since each paddock’s original conversion from scrub/native bush (years); current landuse (pasture or forage crop); mean maintenance and capital P fertiliser inputs (kg ha^{-1}); mean soil test P concentration (Olsen P, mg L^{-1}); mean stocking type and rate (stock units ha^{-1}).

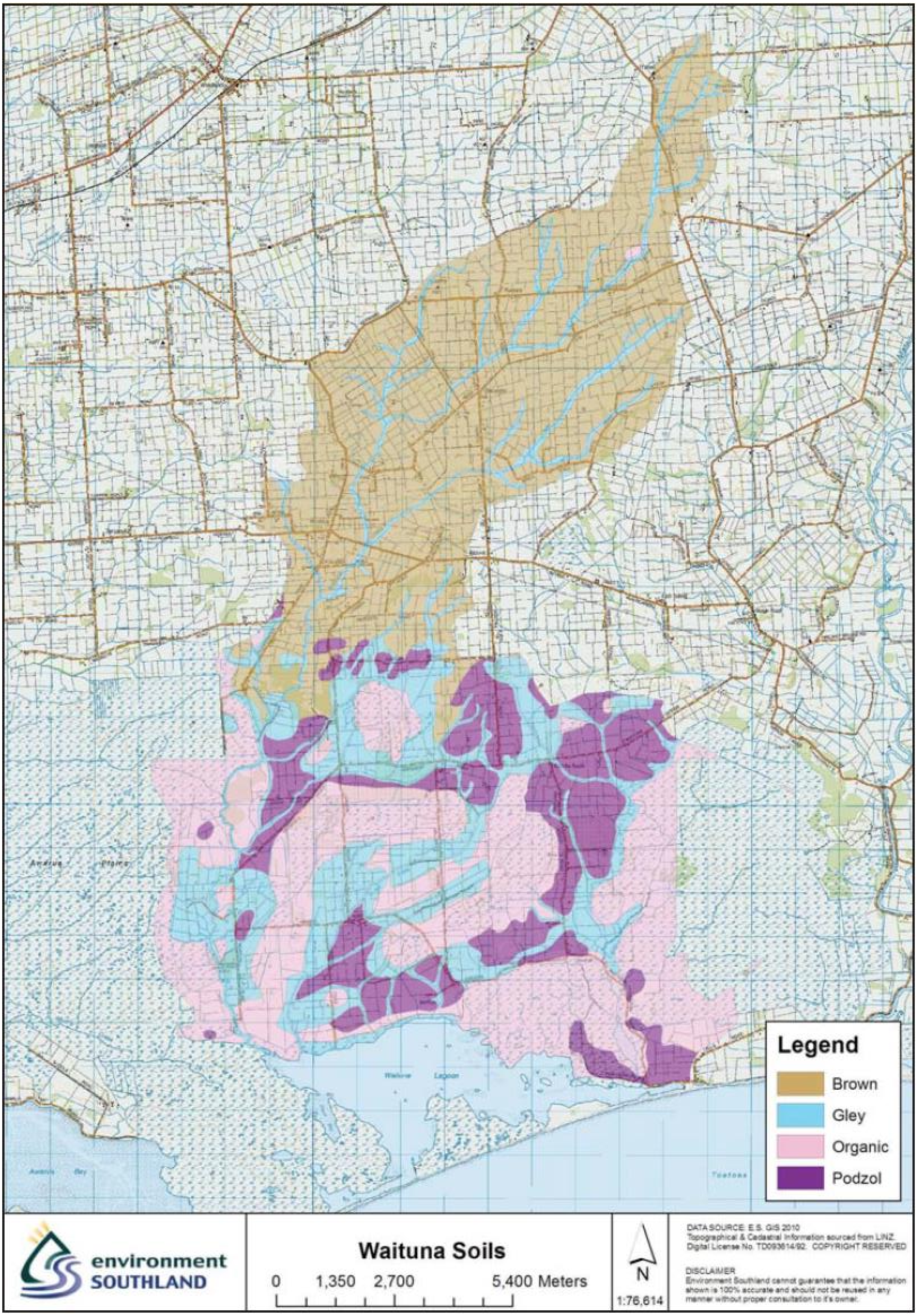

Figure 2.1 Waituna catchment and approximate distribution of soil types (Taken from Environment Southland).

Soil samples were collected in July 2012 from the surface (0-7.5 cm) and from below the plough layer (30-37.5 cm) at each site. Samples were air-dried at 60 °C, ground and sieved < 2 mm. Soils were analysed for pH (in water; Hendershot and Lalande 1993), Olsen P (Olsen et al. 1954), total P (via perchloric-nitric acid digestion; Olsen and Sommers 1982), WEP (McDowell and Condron. 2004), $CaCl_2$-P (McDowell and Condron 2004), degree of phosphate saturation (DPS; via oxalate extractable Al, Fe, Ca, Mn and P; McKeague and Day, 1966; Breeuwsma et al. 1995), organic C (Metson et al. 1979), ASC (Saunders 1965), and bulk density (Parent and Caron 1993).

A mass balance was also conducted to determine how much P had been lost since the paddock was developed. In keeping with McDowell (2008), P losses from 0 – 7.5 cm depth were determined using the model:

$$Loss_n = \sum_{\mathrm{i=0}}^{\mathrm{n}} ([Input_i - Output_i] + Soil_{n=0}) - Soil_{i-n}$$

whereby losses of P are equal to the sum of soil P concentration (kg P ha^{-1}; after accounting for BD) before development ($Soil_{n=0}$; assumed to equal TP in undeveloped sites) and the difference between input and outputs of P from time zero to the year of sampling (kg P ha^{-1}), minus soil P concentration (kg P ha^{-1}) at the time of sampling ($Soil_{i-n}$). Total P off-takes (kg P ha^{-1}) were derived from the Overseer® nutrient budget program (AgResearch 2013) as a function of land use (estimated to be 16 kg P ha^{-1} on average for dairy properties and 1 kg P ha^{-1} on average for drystock properties), while annual and historic P inputs were taken from fertiliser (rate, frequency, type and P percentage) and time since development data collected via individual land owner data. Soil TP and BD data for the mass balance was estimated from samples collected at each site. Plotting the estimated losses against age (n = 1 year) of development, and fitting a simple linear regression, yields a slope equivalent to the mean loss of P (kg ha^{-1} yr^{-1}) with time. Estimates of P loss could not be made for the 30-37.5 cm depth as the quantity of P input via leaching from shallower depths was unknown.

Summary statistics (mean, standard error, range, and probability), k-means clustering and regression modelling were determined using R version 3.0.1 (R Core Team 2013), and best subsets regression modelling with Mallows Cp was carried out using Minitab (Release 16.2.2, Minitab 2010). Data was log-transformed if not normally distributed. The threshold for statistical significance was $P < 0.05$.

2.3 Results and Discussion

2.3.1 Attributing soil properties to potential P losses

A *k*-means cluster analysis (Forgy 1965) of topsoils and subsoils was carried out to determine similarities between samples at each depth using the parameters TP, Olsen P, BD, pH, C:N ratio, and oxalate-extractable Al, Ca, Fe, Mn and P concentrations. Clustering split samples into two distinct clusters (C1 and C2) that had a high proportion of either Organic (C1) or Podzol (C2) soils (Table 2.1). The two clusters were found to explain 59.7% of the variability in the data set (Figure 2.1). Topsoils were evenly distributed within each cluster, comprising 47% and 53% topsoils in clusters C1 and C2, respectively. However, C1 had a greater proportion of subsoils than C2 (66%). Of the samples comprising C1 and C2, 79.2% and 76.2% were top and subsoils from the same paddock, respectively. The results indicated that significant differences existed between soil types, but not between the depths sampled, and justified combining topsoils and subsoils for further comparison of P loss by soil type.

Table 2.1. Output of the cluster analysis from Figure 2.1, showing the proportions of Organic and Podzol soils, and topsoils and subsoils in each cluster

Cluster	Organic	Podzol	Composition (Soil Order)	Topsoils	Subsoils	Composition (Sample depth)
1	49	13	79.0% Organic	26	36	41.9% topsoils
2	6	41	87.2% Podzol	29	18	61.7% topsoils

Organic soils contained lower mean TP, BD and ASC values, but greater Olsen P, WEP, C and $CaCl_2$-P concentrations compared with Podzol soils (Table 2.2). This is consistent with the increase in WEP with increasing Olsen P or decreasing ASC (McDowell and Condron 2004; Figure 2.2a,b). The enrichment of mean $CaCl_2$-P in Organic compared to Podzol soils was attributed to mean concentrations of Al_{ox} and Fe_{ox} that were two to four times greater (respectively) and C concentrations three times lower in Podzol compared to Organic soils. Nine of the ten soils that returned the greatest $CaCl_2$-P concentrations were Organic soils (Figure 2.2c), with a low mean pH (< 3.5) and ASC (< 11%), but were rich in C (> 450 g C kg^{-1}). At pH < 3.5, sorption to Fe and to a lesser extent Al is an important mechanism for P retention (Lindsay 1979; Murphy and Stevens 2010; Gustafsson et al. 2012). In these soils both Al_{ox} and Fe_{ox} were relatively low (Al_{ox} < 840 mg kg^{-1}, Fe_{ox} < 1,700 mg kg^{-1}); hence, there was little potential for stable P-complexes to form. In addition, the high C concentration of the soil creates competition between dissolved organic carbon (DOC) compounds and orthophosphate ions, further limiting the ability of the soils to retain P (Mengel 2008). The poor potential to retain P was further demonstrated by a low mean TP (201 mg kg^{-1}), despite receiving mean P inputs of 282 kg ha^{-1} over the 7 years (on average) since development.

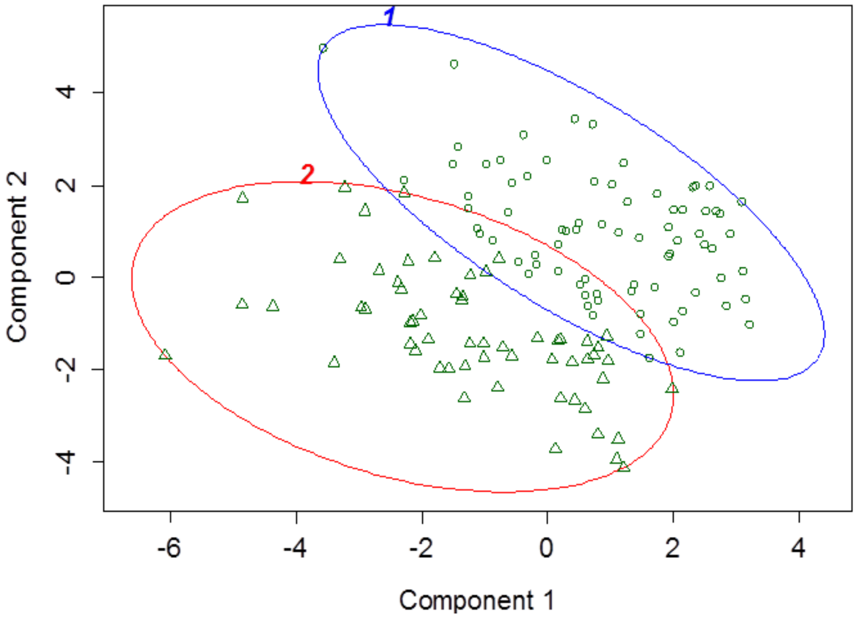

Figure 2.2. The distribution of Organic and Podzol soils within Cluster 1 and Cluster 2 (circles and triangles represent Organic and Podzol soils, respectively). The two clusters explain 59.66% of the variability in the data set.

McDowell and Sharpley (2001) found that $CaCl_2$-P and WEP provided a good approximation of the potential for P losses in subsurface and surface runoff, but did not include any Organic soils in their work. Indeed, to the author’s knowledge, my data is the first to report $CaCl_2$-P or WEP in Organic soils under intensive dairying. There is a strong likelihood that P losses will occur via sub-surface runoff due to high porosity and hydraulic conductivity, and low ASC. These factors result in enhanced interaction and the release of P from the soil into soil solution (Stutter et al. 2005). For example, data for Organic soils of very low ASC (< 5%) in Southland, New Zealand have shown DRP concentrations in the order of 3-10 mg L^{-1} in drainage water under forage crops grazed by dairy cattle (McDowell and Monaghan 2014).

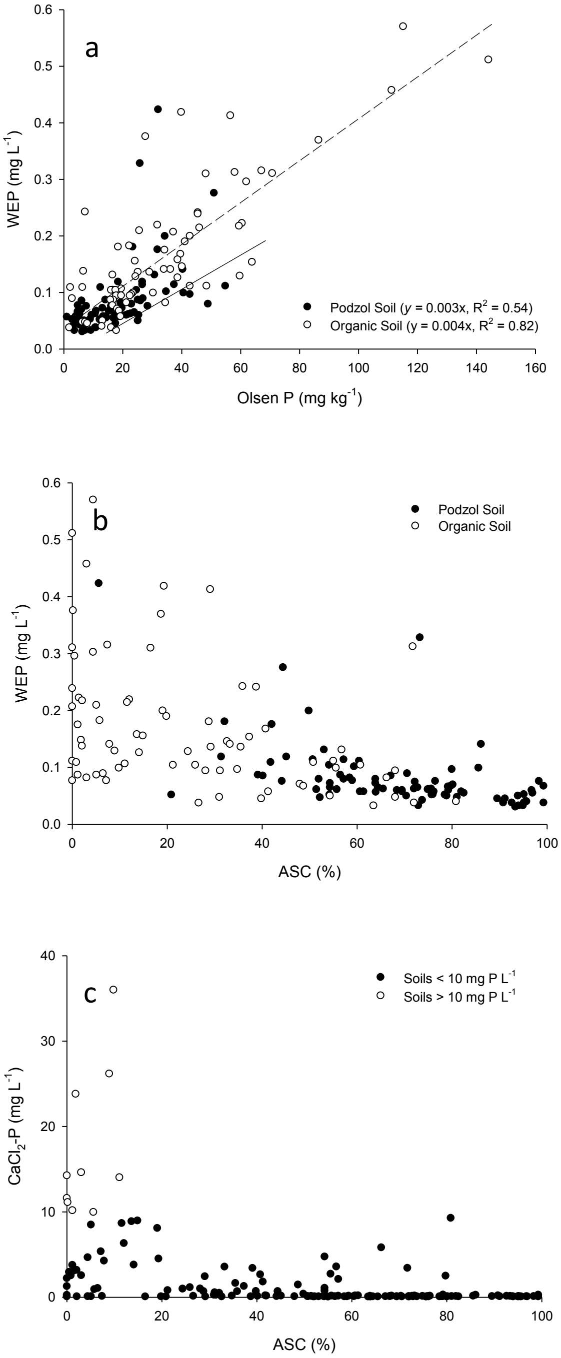

Figure 2.3. Plot of WEP concentration against Olsen P concentration (a) or ASC (b) and $CaCl_2$-P against ASC (c) for Organic and Podzol soils.

Table 2.2. Mean, minimum and maximum and standard errors for selected physio-chemical properties for Organic and Podzol topsoils and subsoils.

Soil Order, depth and statistic	Total P (mg kg^{-1})	Olsen P (mg L^{-1})	Bulk density (g cm^{3})	WEP (mg L^{-1})	CaCl$_2$-P (mg L^{-1})	ASC (%)	pH	C (g kg^{-1})	Al* (mg kg^{-1})	Ca* (mg kg^{-1})	Fe* (mg kg^{-1})	Mn * (mg kg^{-1})	Paddock age (yrs)
Topsoil (0-7.5 cm)													
Organic (n = 38)													
Range	87-1285	6-144	0.19-0.83	0.08-0.57	0.01-9.92	1-68	3.6-6.3	91-500	364-10,758	14-50	249-7,325	1-92	1-27
Mean	756	45.3	0.47	0.23	1.94	24	4.6	359	2,291	24	2,082	20	8
Std. error	46	5	0.03	0.02	0.44	3	0.1	18	323	1	294	4	1
Podzol (n = 40)													
Range	247-2331	3-54	0.48-1.05	0.05-0.22	0.020-4.71	2-99	3.9-6.4	51-453	713-18,472	18-275	543-15,137	1-110	7-60
Mean	1039	24.2	0.78	0.09	0.5	65	4.9	146	7,062	44	4,761	23	38
Std. error	61	2	0.02	0.01	0.28	3	0.1	13	529	6	500	3	3
Sub-soil 30-37.5 cm													
Organic (n = 36)													
Range	102-1108	2-59	0.19-1.05	0.04-0.31	0.02-35.96	1-93	3.2-4.9	13-530	420-13,005	17-38	116-6,429	1-27	1-27
Mean	366	22.5	0.64	0.1	5.29	37	3.7	342	3,470	24	1,363	3	8
Std. error	41	3	0.03	0.01	1.35	4	0.1	26	567	1	237	1	1
Podzol (n = 41)													
Range	180-1032	1-49	0.56-1.18	0.03-0.08	0.02-0.23	31-99	4.0-6.0	18-350	882-22,822	18-109	476-12,507	1-88	7-60
Mean	518	10.7	0.91	0.05	0.08	82	4.5	110	10,859	35	5,174	11	38
Std. error	55	1	0.03	0.01	0.01	3	0.1	11	798	3	538	3	3

*Ammonium oxalate extractable

2.3.2 Predicting WEP and $CaCl_2$-P

As a first step in predicting WEP and $CaCl_2$-P, Pearson correlation coefficients were generated for physio-chemical properties for Organic and Podzol soils (Table 2.3). There were commonalities among coefficients for the two soil Orders. In general, correlations with WEP were positive for DPS, Olsen P, C and N, and negative with Al_{ox}, ASC, and BD.

DPS is commonly used as an indicator for the potential of soil to release P to surface runoff and leaching (viz. subsurface runoff), so the correlation of WEP with high soil P saturation is to be expected (Allen and Mallarino 2006; Amarawansha and Indraratne 2010). Water extractable P has also been demonstrated to have a close relationship with Olsen P (McDowell and Sharpley 2001), but without accounting for P sorption capacity via ASC, the relationship is generally curvilinear over a wide range of Olsen P concentrations. High WEP concentrations in soils enriched with C has been shown to be caused by organic anions out-competing P for soil sorption sites, particularly at low pH (Sibanda and Young 1986; Guppy et al. 2005). The correlation between N and WEP can be best explained by referring to Cleveland and Liptzin (2007), who note that the biogeochemical cycles of C and N are linked due to the requirement for N to fuel the growth of plant matter that ultimately contributes to soil C content. This implies that while N is not directly influential to WEP, high concentrations of N and C are likely to coincide, and therefore cause a correlation of N with WEP.

A significant negative relationship occurred between WEP and Al_{ox}, which is not surprising as Al_{ox} forms part of the quotient in DPS (i.e. as a surrogate estimate of P sorption capacity). Oxalate extractable Fe, also used in calculating the DPS, was not significantly correlated with WEP, presumably since Fe is much more sensitive to anaerobic conditions and can be more readily leached from the soil than Al (Pant et al. 2002).

The next stage in predicting WEP and $CaCl_2$-P used a step-wise regression for each soil Order. For Podzol soils, the step-wise regression prediction that accounted for the most variation in WEP included the quotient of Olsen P and ASC and N concentration ($P < 0.001$; adj. $R^2 = 0.95$; Eq. 1).

Table 2.3. Pearson correlation coefficients between WEP or $CaCl_2$-P and selected physiochemical properties for Organic and Podzol topsoil and subsoils and associated *P*-values (bold if significant).

Physiochemical property	WEP$_{ORG}$	*P*	WEP$_{POD}$	*P*	$CaCl_2$-P$_{ORG}$	P	$CaCl_2$-P$_{POD}$	*P*
Total C (g kg^{-1})	0.410	**0.000**	0.523	**0.000**	0.442	**0.000**	0.440	**0.000**
ASC (%)	-0.404	**0.000**	-0.537	**0.000**	-0.311	**0.003**	-0.407	**0.000**
DPS (%)	0.748	**0.000**	0.590	**0.000**	-0.176	0.109	0.466	**0.000**
Total N (g kg^{-1})	0.625	**0.000**	0.665	**0.000**	0.119	0.28	0.536	**0.000**
Bulk density (g cm^3)	-0.528	**0.000**	-0.495	**0.000**	-0.147	0.182	-0.276	**0.012**
Olsen P (mg L^{-1})	0.813	**0.000**	0.544	**0.000**	-0.014	0.899	0.142	0.203
Al* (mg kg^{-1})	-0.231	**0.034**	-0.426	**0.000**	-0.243	**0.025**	-0.253	**0.021**
Fe* (mg kg^{-1})	-0.187	0.088	-0.416	**0.000**	-0.255	**0.019**	-0.176	0.113
pH	0.203	0.064	0.314	**0.002**	-0.381	**0.000**	-0.002	0.986
Total P (mg kg^{-1})	0.449	**0.000**	0.146	0.190	-0.406	**0.000**	0.146	0.19
P* (mg kg^{-1})	0.174	0.113	0.068	0.543	-0.328	**0.002**	-0.004	0.971
Ca* (mg kg^{-1})	0.346	**0.001**	0.041	0.714	-0.196	0.073	-0.005	0.964
Years since development	-0.025	0.821	-0.141	0.206	0.013	0.906	-0.121	0.278
Mn* (mg kg^{-1})	0.144	0.191	0.109	0.329	-0.221	0.043	0.045	0.688
CaCl2-P (mg L^{-1})	-0.110	0.319	0.547	**0.000**	-	-	-	-
WEP (mg L^{-1})	-	-	-	-	-0.110	0.319	0.547	**0.000**

* Ammonium oxalate extractable

$$WEP_{Pod} = 0.067 \times \text{Olsen P/ASC} + 0.003 \times N + 0.030 \qquad \text{[Eq. 1]}$$

Nitrogen, although a component of the model, was not highly influential; hence, it could be argued that the relationship reverts to just the quotient of Olsen P and ASC. The Olsen P/ASC quotient was also included in the regression output predicting $CaCl_2$-P concentration ($P < 0.001$; adj. $R^2 = 0.72$; Eq. 2).

$$CaCl_2\text{-}P_{Pod} = 1.80 \times \text{Olsen P/ASC} - 0.167 \qquad \text{[Eq. 2]}$$

The use of the quotient is consistent with past work estimating DRP concentrations in surface (WEP) and sub-surface ($CaCl_2$-P) runoff (McDowell and Condron 2004), and demonstrates that the Podzol soils examined in this paper conform to the concept that the potential for P losses are a function of the quantity of P in the soil (as approximated by Olsen P) relative to the soils P sorption capacity (as approximated by ASC). For WEP_{Pod}, the slope of 0.14 ($P < 0.001$; $R^2 = 0.78$) attributed to the quotient of Olsen P/ASC was steeper to that determined for more mineral soils in McDowell and Condron (2004), at 0.03 ($P < 0.001$; $R^2 = 0.83$).

For Organic soils, the best prediction of WEP included terms for DPS, Olsen P and C ($P < 0.001$, Adj. $R^2 = 0.84$; Eq. 3).

$$WEP_{Org} = 0.005 \times DPS + 0.003 \times \text{Olsen P} + 0.0001 \times C - 0.025 \qquad \text{[Eq. 3]}$$

The greatest influence on WEP_{org} concentrations within the step-wise prediction was accounted for by the DPS and then Olsen P. The DPS is derived as the molar quotient of oxalate-extractable P to the sum of Al, Fe, and Ca (McKeague and Day 1966; Breeuwsma et al. 1995). In essence the test is similar to ASC as it indicates the ratio of the amount of P already sorbed to the maximum P sorption capacity of the soil. However, the DPS test utilises a much more acidic extraction (pH 3) compared to the ASC test (pH 4.6 Saunders 1965) and therefore may better suit those constituents controlling WEP_{org} in the acidic Organic soils (Table 2.2). Although C concentration was significant, it did not exhibit a great deal of influence within the regression.

Calcium chloride extractable P concentration was not predicted by any variable for Organic soils. Concentrations of $CaCl_2$-P were much more variable than WEP concentrations (Table 2.4). Clearly, data shows that $CaCl_2$ extracts different quantities of P compared to water, but McDowell et al. (2002) also showed that it extracted P from different pools. However, the use of $CaCl_2$-P as a measure of sub-surface losses has not been verified for Organic soils (McDowell and Condron 2004). Hence, before any additional work occurs to predict $CaCl_2$-P from a wider set of variables than used here, it must be determined if $CaCl_2$-P is a useful measure of estimating sub-surface losses from Organic soils.

2.3.3 Influence of time since development

Data showed that the greatest WEP concentrations were from Organic soils that had been developed within 10 years (Figure 2.3). A significant negative relationship between WEP and years since development was detected for combined topsoils of both soil Orders ($P < 0.001$, $R^2 = 0.22$), but not for individual soil Orders: Organic ($P = 0.001$, $R^2 = 0.74$) or Podzol ($P = 0.01$, $R^2 = 0.52$). The lack of a significant relationship with years since development was found to be the case for the majority of the parameters measured (Table 2.5); with the exception of increasing Organic soil bulk density (likely due to ongoing compaction and C mineralisation) and decreasing Podzol soil Fe concentration with time. The limited effect of time may have been due to a restricted spread of the data by soil Order, particularly for Organic soils, where the majority of soils were under 25 years since development.

Plotting the estimated cumulative P loss (from the mass balance model) against the number of years since development enabled the mean annual P loss from the 0-7.5 cm layer for each of the soils Orders to be calculated using the slope of the regression. A Chow test (Chow 1960) strongly indicated that slopes were different from one another ($P = 0.05$). On average, 38 kg P ha^{-1} $year^{-1}$ was being lost from Organic topsoils and 21 kg P ha^{-1} yr^{-1} from Podzol topsoils. However, it should be noted that while the mass balance shows P is being lost, it does not stipulate where the P is being lost to, which is likely to be a combination of transfer to other parts of the farm by stock, deeper soil layers and to runoff, as influenced by soil physicochemical properties.

Table 2.4. Coefficient of variation values of Organic and Podzol topsoil and subsoil for selected physio-chemical properties.

	Total P ($mg\ kg^{-1}$)	Olsen P ($mg\ L^{-1}$)	Bulk density ($g\ cm^{3}$)	WEP ($mg\ L^{-1}$)	$CaCl_2$-P ($mg\ L^{-1}$)	ASC (%)	pH	C ($g\ kg^{-1}$)	Al ($mg\ kg^{-1}$)	Ca ($mg\ kg^{-1}$)	Fe ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Paddock age (yrs)
Organic topsoil	38	65	36	53	135	96	17	30	86	37	85	119	68
Organic subsoil	72	67	33	55	133	86	15	48	100	43	106	139	70
Podzol topsoil	42	44	17	58	267	29	12	59	42	42	60	93	44
Podzol subsoil	71	86	18	44	71	23	15	65	47	118	69	167	46

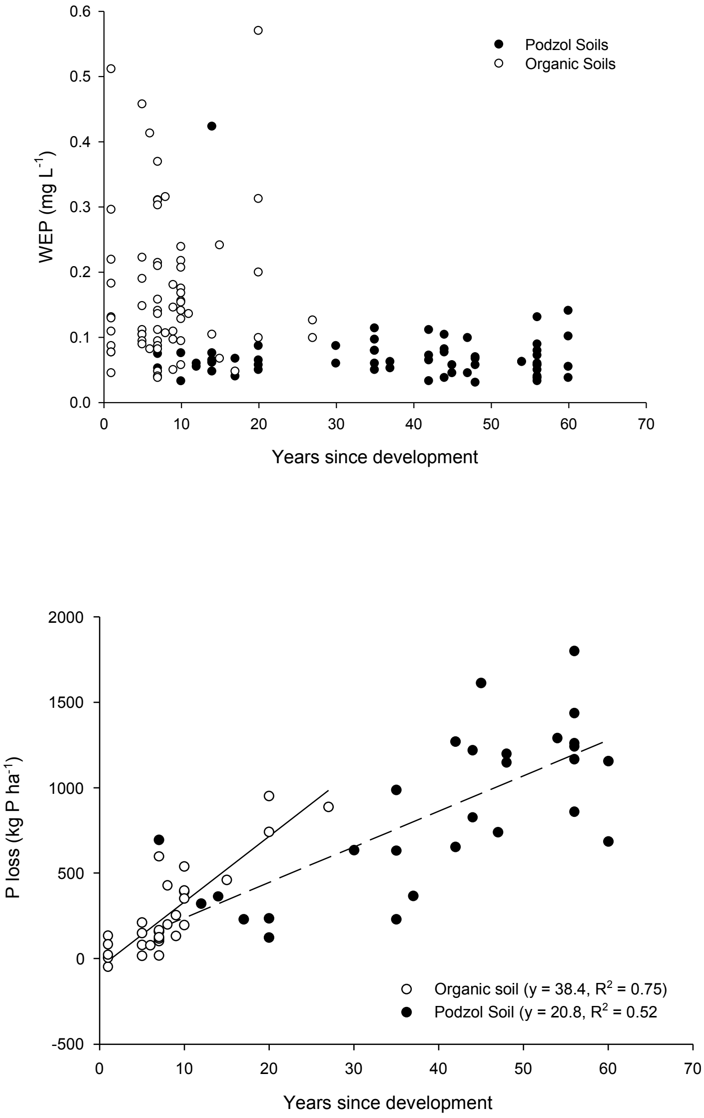

Figure 2.4. Plot of WEP concentration (top) and P loss (bottom) against years since development for Organic and Podzol soils. The slope and coefficient of determination for the regression fits to the Organic and Podzol soil data are also given.

Table 2.5. Correlation coefficients between years since development and selected physiochemical properties for Organic and Podzol topsoils and subsoils, and associated *P*-values (bold if significant).

Physiochemical property	Years since development (Org)	P	Years since development (Pod)	P
Al* (mg kg^{-1})	0.047	0.81	0.056	0.69
ASC (%)	0.234	0.23	0.081	0.56
Bulk density (mg L^{-1})	0.531	**0.00**	-0.262	**0.06**
Total C (g kg^{-1})	0.019	0.92	0.229	0.10
Ca* (mg kg^{-1})	0.020	0.92	-0.037	0.79
$CaCl_2$-P (mg L^{-1})	0.013	0.91	-0.121	0.28
Fe* (mg kg^{-1})	0.066	0.74	-0.293	**0.03**
Mn* (mg kg^{-1})	0.133	0.50	-0.026	0.85
Total N (g kg^{-1})	0.008	0.97	0.211	0.13
Olsen P (mg L^{-1})	-0.022	0.91	0.133	0.34
P* (mg kg^{-1})	0.171	0.38	0.128	0.36
pH	0.216	0.27	-0.214	0.12
Total P (mg kg^{-1})	0.109	0.58	0.126	0.36
WEP (mg L^{-1})	-0.025	0.82	-0.141	0.21

*Ammonium oxalate extractable

Past estimates using this mass balance approach have recorded similar P losses of 20 kg P ha^{-1} year^{-1} from a Recent Soil (Hari Hari silt loam) (McDowell 2008). In the present study, the quantity of P estimated lost annually from the Organic topsoils far exceeds the estimates for Podzols, but is not unexpected given the Organic soils likely greater infiltration rate (via low BD), frequency of anaerobic conditions and poor P sorption compared to the Podzols (Table 2.2). The installation of artificial drainage has also been well documented to result in increased losses of P from topsoil to surface waters. For instance, Miller (1979) reported losses of up to 37 kg P ha^{-1} year^{-1} from Organic soils in Ontario, Canada, while rates of up to 168 kg P ha^{-1} year^{-1} were reported from Organic wetland soils in Central Florida by Reddy (1983). Losses as high as those reported here and internationally highlight the role of Organic soils as potentially point sources of P loss if managed for intensive agricultural production and remedial measures should be put in place to ensure that losses do not impair freshwater.

2.4 Conclusion

The findings of this study highlighted the high potential for P losses from recently developed compared to undeveloped Organic soils, but that the potential for this loss can be estimated from a soil test or estimated from associated soil tests and characteristics. Such tests (or their predictions) may be used to help identify Organic and Podzol soils that pose a risk to surface water quality from P losses.

Chapter 3

The effect of soil moisture extremes on the pathways and forms of phosphorus loss in runoff from two contrasting soil types

3.1 Introduction

As the price and competition for suitable pastoral land increases, more marginal land is developed for intensive agriculture (Ehrlich and Holdren 1971; Asner et al. 2004). The availability of P for export from soils is largely a function of a soil's mineral content, moisture regime, oxidation-reduction processes and pH. These properties differ substantially between Organic and Brown soils (Histosols and Inceptisols; USDA). For example ASC, outside of soil P concentration, is the main factor influencing the availability of P loss in soils (McDowell and Condron 2004) and is regulated by concentrations of metal oxides (minerals) that bind inorganic P, decreasing its transport in soil solution (Zak et al. 2004). The mineral content of many Organic soils is typically very low, while concentrations of organic matter and dissolved organic carbon (DOC) are high: DOC can compete with orthophosphate ions for sorption sites on the soil (Guppy et al. 2005). In catchments with marginal land, Organic and Brown soils can appear adjacent to one another. However, given their physiochemical differences it is important to quantify the relative pathways of P loss so that site-specific strategies to mitigate P loss (and the effect on surface water quality) can be made more cost-effective.

Phosphorus loss pathways via runoff include surface runoff and subsurface flow, which are influenced by factors such as infiltration rates (Lal et al. 1989), soil water storage (i.e. pore space) and preferential flow paths. Organic soils have a high infiltration rate where subsurface flow (leaching) is expected to be the major pathway of P loss. Surface runoff could occur, but is unlikely unless the artificial drainage network is overwhelmed and saturation-excess surface runoff results. Brown soils exhibit a greater bulk density and lower hydraulic conductivity (and pore space) meaning surface runoff is likely to be the dominant pathway of P loss. However, under very dry conditions, water repellence; or hydrophobicity can be extremely high in Organic soils. This increases the likelihood of infiltration-excess surface runoff of P. Deurer et al. (2011) compared hydrophobicity in 50 grassland sites spanning the 10 most dominant New Zealand soil orders. Organic and Podzol soils were found to exhibit the highest degree, and persistence, of water repellency, due to the high concentration of hydrophobic organic matter and the much lower proportion of soil hydrophilic matter exposed to water. Seasonal soil drying causes hydrophobicity in 70% of New Zealand top soils (Deurer and Müller 2010), which suggests that infiltration-excess surface runoff could well occur in Organic soils in summer and autumn. This is of particular concern as it means that runoff will transport P during summer when the potential for water quality impairment (e.g. via algal growth) is greatest (McDowell 2012). There is also evidence to indicate that increased infiltration-excess surface runoff (as opposed to drainage or saturation-excess surface runoff) has more energy and results in the erosion of particulate P, which will degrade water quality in lotic systems (Kleinman et al. 2009).

Strategies to mitigate the loss of P from land to water tend to focus on reducing the quantity of P in the soil such as maintaining soil Olsen P concentrations at no more than the agronomic optimum (McDowell et al. 2003a) and not on transport processes. However, transport processes can dominate the load (i.e. concentration by flow) of P lost. Under extreme conditions, transport via hydrophobicity or saturated conditions could therefore result in P losses that are likely to impact surface water quality even if soil Olsen P is low.

Little is known of how antecedent moisture contents influence the pathways and forms of P losses in runoff from soils of highly contrasting chemical and physical composition. More specifically, I contrasted two soils from a catchment recently developed into intensive pastoral agriculture – and therefore likely to have a range of soil Olsen P concentrations despite recommendations to avoid concentrations in excess of the agronomic optimum. The two soil orders chosen were a Brown and Organic soil with optimums for pasture production around 25 and 40 mg Olsen P L^{-1}, respectively (Roberts and Morton 2009). My hypotheses were that: 1) rainfall applied to a dry soil would cause greater particulate P losses in surface runoff, due to hydrophobicity; 2) P losses from a wet soil would be via dominated by subsurface flow and filtered P; and 3) that both runoff processes would result in environmentally unacceptable P losses at agronomically productive Olsen P concentrations depending on the sorption capacity (viz. ASC) of the soil.

3.2 Materials and Methods

3.2.1 Soils

The Waituna catchment lies approximately 20 km southeast of Invercargill, New Zealand. It has a surface area of 21,000 ha (Schallenberg et al. 2010) and drains into the Waituna Lagoon via a RAMSAR classified wetland (Thompson and Ryder 2003). Soil types range from well-drained Brown soils to poorly-drained Organic, Gley and Podzols (Wilson 2011). Farming in the Waituna catchment is dominated by dairying, which covers c. 80% of pastoral land in the catchment (Risk 2011). Of these dairy farms, around 25 are situated in the southern portion of the catchment where Organic soils (including Podzols and Gleys with Organic-like topsoils) are dominant, but are also commonly adjacent to Brown soils.

Soils (Invercargill peat, a mesic acid Organic soil and a Mokotua; firm mottled Brown soil; Hewitt 2010) were collected from below the plough layer at 30 – 60 cm depth to ensure soils were of similarly low Olsen P concentrations. The Organic soil had been used the previous year for a forage crop of Swede (*Brassica napobrassica*) and had received no fertiliser or lime amendments in the nine months prior to soil collection. The Brown soil was under permanent pasture and had not been grazed by sheep for three months nor received fertiliser amendments. The Olsen P concentration of the Organic and Brown soils was 11 and 7 mg L^{-1}, respectively (Table 3.1). Soils for chemical analyses were air-dried, crushed and passed through a 2-mm sieve for pre- and post-runoff analysis of ASC (Saunders 1965), TP (< 1mm, using perchloric acid digestion with an additional HNO_3 digestion step to oxidise organic matter) (Olsen and Sommers 1982), Olsen P (Olsen et al. 1954), BD (Parent and Caron 1993) and pH (Hendershot and Lalande 1993). The potential for P loss to surface and subsurface flow were determined using WEP and $CaCl_2$-P, respectively (McDowell and Condron 2004).

Table 3.1. Selected physicochemical characteristics of the unaltered soils.

	-------------------- Phosphorus extracts --------------------				--------------------- Soil physiochemical properties ---------------------					
Soil Order	Olsen P (mg L^{-1})	WEP (mg L^{-1})	CaCl$_2$-P (mgL^{-1})	Total P (mg kg^{-1})	Bulk density (g cm^{3})	pH	C (%)	ASC (%)	Water drop penetration time (s^{-1})	
									Dry	Wet
Organic	11	0.14	5.33	509	0.31	4.2	37.6	5	>3600	<5
Brown	7	0.10	0.02	186	0.91	5.0	7.9	58	<5	<5

3.2.2 Runoff boxes and rainfall simulator

Sixty runoff boxes (Figure 3.1) were used in this trial. Boxes were 800-mm long by 200-mm wide by 70-mm deep, with six 2-mm holes drilled in the bottom to enable collection of subsurface flow (thereafter called leachate). Soil was placed into boxes and packed close to field bulk density (McDowell et al. 2003). The sixty boxes represented three replicates of five fertiliser rates by two (90% and <10% of available water holding capacity, AWHC) moisture treatments for each soil type. The fertiliser rates were designed according to the capital application of P required to increase mineral and peat soil Olsen P concentrations to control, 15, 40, 60 and 80 mg P L^{-1} (Roberts and Morton 2009). This equated to rates of 0, 0.21, 0.42, 0.63 and 0.84 g P box^{-1} for Brown soils, and 0, 0.21, 0.56, 0.84 and 1.13 g P box^{-1} for Organic soils. Superphosphate was sieved (< 1 mm) before being applied. Spiked soils were watered to near field capacity then left to air dry for one week and then wet and dried again to ensure SSP had equilibrated with soil. During week four (three weeks after SSP application), ryegrass was sown at a rate of 22 kg ha^{-1} (Young et al. 2010) and soils watered daily to retain moisture until germination without causing drainage. During week six, fortnightly additions of 10 mm of ¼ strength P-deficient Hoagland solution began (Hoagland and Arnon 1950). Three weeks after germination, ryegrass was trimmed to a dry matter residual of 1500 kg ha^{-1}. Timing was repeated at monthly intervals. Irrigation was stopped 12 weeks after SSP application and boxed soils allowed to dry to either 90% or <10% of AWHC. The AWHC was calculated using bulk density and volumetric soil moistures calculated from saturated and air-dry soil cores collected at the same time as soils (Curran Cournane et al. 2010). Each box was weighed and moisture adjusted to ensure that treatments were at the correct moisture level before runoff was induced.

A water repellency assessment was carried out using the water drop penetration time (WDPT) test of DeBano (1981) on air-dried soil samples and soils in runoff boxes before they were rained upon. To do this, a single water drop was placed on the sample surface, and the time it took to absorb was recorded. This was repeated five times for each treatment. Five water repellency classes were used, in line with studies by Biemelt et al. (2005). These were WDPT <5 s^{-1} = wettable/non-water repellent, 5–60 s^{-1} = slightly water repellent, 60–600 s^{-1} = strongly water repellent, 600–3600 s^{-1} = severely water repellent, and >3600 s^{-1} = extremely water repellent.

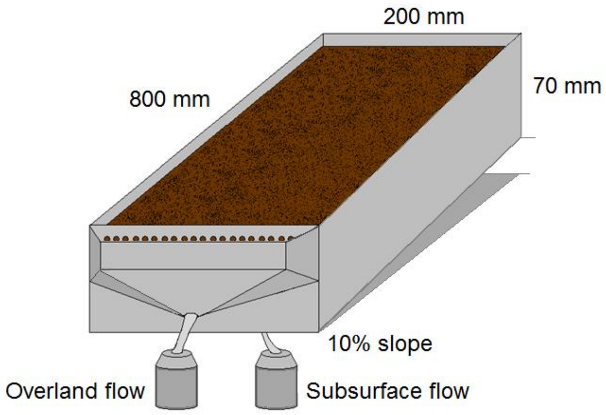

Figure 3.1. Design of runoff box showing integrated surface and subsurface flow samplers.

Boxes were inclined at a slope of 10% and runoff generated using tap water via an artificial rainfall simulator (< 0.005 mg P L^{-1}) to deliver rainfall at a rate of 30-35 mm h^{-1}. This was designed to simulate storm conditions with an annual return interval of 5 years (calculated for the Waituna Catchment using NIWA’s High Intensity Rainfall System V3; NIWA 2010). The rainfall simulator was constructed as a 3.05 m^3 aluminium frame with rainfall delivered from one TeeJet 1/4HH-SS30WSQ nozzle (Spraying Systems Co., Wheaton, IL) approximately 250 cm above the soil surface. A previous trial by McDowell et al. (2007) employed this simulator and found the drop-size, velocity and impact energies of droplets to be closely representative of natural rainfall. The elapsed time for surface runoff and leachate to occur was noted, and samples collected for 40 minutes. The volume of runoff via both pathways was recorded and sub-samples taken for laboratory analysis.

3.2.3 Runoff analysis

Samples of runoff were filtered (0.45 µm) immediately after collection and were analysed for FRP within 24 h. Filtered and unfiltered samples were also acid persulphate digested and P determined within 7 days (Eisenreich et al. 1975; Rowland and Haygarth 1997). This yielded TFP and TP, respectively. All P determinations were made colorimetrically using the method of Watanabe and Olsen (1965). Filtered unreactive P and PP were calculated as the difference between TFP and FRP, and TP and TFP, respectively. Suspended sediment was analysed by filtering a known volume of a sample, then weighing the oven-dried residue on a GFA filter paper (0.7 µm pore size) of pre-determined weight.

3.2.4 Statistical analysis

An analysis of variance (ANOVA) was used to compare soil data surface runoff and leachate P losses between treatments. Data was tested for normality and log-transformed where necessary. Due to non-constant variation in phosphate fractions (concentrations and losses) and volumes in runoff, data was log transformed, followed by a Tukey multiple comparison test between soil and moisture means.

3.3 Results and Discussion

3.3.1 Soil extractable P before and after runoff

In line with other studies (e.g. Sharpley 1995; Lourenzi et al. 2014), before-runoff soil extractable P concentrations increased with target Olsen P for all treatments and soils (Table 3.2). Before runoff the Organic soil generally had greater $CaCl_2$-P and WEP concentrations, but lower Olsen P and TP concentrations than the Brown soil. The greater soil TP concentration reflects a larger pool of native P present in the Brown compared to Organic soil before soils were fertilised. In contrast, the greater WEP and $CaCl_2$-P concentrations in the Organic compared to Brown soils relates to much lower ASC (and hence P sorption capacity; McDowell and Condron 2004) of Organic soil. In most cases, extractable P concentrations of both soils decreased after runoff. However, the P lost from the soils after one runoff event was not great enough to significantly alter the frequency and strength of treatment differences in extractable P concentrations.

3.3.2 Runoff volumes

For the Organic soil, more surface runoff was generated under dry than wet conditions (Figure 3.2). Surface runoff produced under dry conditions was most likely due to hydrophobicity, as the water droplet penetration test classified the soil as 'extremely water repellent' (Table 3.1; Biemelt et al. 2005). The volume of surface runoff generated from the Organic soil under dry conditions was similar to that produced from the Brown soil under wet conditions, except that surface runoff from the Brown soil was likely caused by saturation-excess surface runoff - produced as the available pore space was filled.

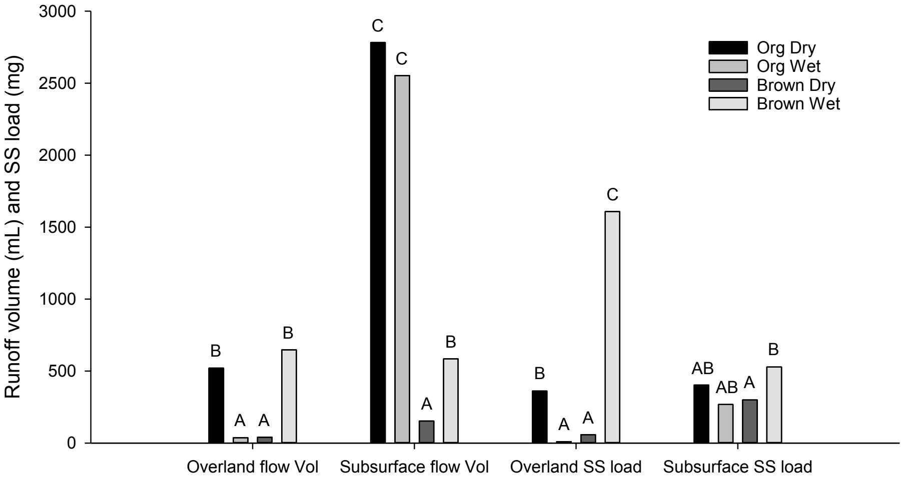

Figure 3.2. Mean runoff volumes and suspended sediment losses for wet and dry Organic and Brown soils. Different letters indicate a significant difference between groups ($P < 0.05$; ANOVA and then Tukey's multiple comparison tests).

The lack of surface runoff and sub-surface flow from the dry Brown soil indicated it was highly wettable and therefore retained much of the rainfall applied (Dekker and Ritsema 2000;

Täumer et al. 2005). Much greater wettability and soil water storage may also explain why volumes of sub-surface flow from the Brown soil were lower than from the Organic soil where high hydrophobicity and macroporosity (due to low density) may have also facilitated flow through the Organic soil (Schwarzel et al. 2002).

3.3.3 Suspended sediment losses

Surface runoff was characterised by high mean SS losses (Figure 3.2). However, while the volume of surface runoff from the dry Organic soil was similar to the wet Brown soil, surface runoff from the wet Brown soil transported three times more sediment (by weight) than dry Organic soil. Furthermore, while sub-surface flow volumes from wet and dry Organic soils were seven times greater on average than Brown soils (Figure 3.2), there were little difference in SS losses. This does not infer that Brown soils and more erodible than Organic soils. In contrast, studies have shown Organic matter-rich soils in the North Island of New Zealand to be highly erodible (Selby 1972). Moreover, the lack of any difference in SS losses is probably due to the gravimetric determination of SS and the much lower weight of Organic material compared to mineral soil particles.

3.3.4 Phosphorus losses

Irrespective of antecedent moisture conditions, mean FRP, FUP, PP and TP concentrations in subsurface flow from Organic soils were 447, 12, 10 and 73 times greater than Brown soils, respectively (Table 3.3). The large differences are primarily because the Brown soil contained a much greater concentration of metal-oxides that can sorb orthophosphate anions than the low ASC Organic soil (Table 3.1; Sims et al. 1998). Differences translated into a similar picture with losses (Table 3.4) largely because, compared to the Brown soil, the Organic soil was packed to a much lower bulk density (representative of field conditions) that would likely have a very high hydraulic conductivity allowing sub-surface flow to occur. In addition, the Organic soil would likely contain greater quantities of negatively-charged humic substances that can compete with P for sorption (Gu et al. 1994), resulting in an elevated potential for P loss – although concentrations of humic materials were not measured.

Compared to sub-surface flow, much less P was transported in surface runoff from the Organic soil – although the concentrations were similar (Table 3.3). This implies surface runoff and sub-surface flow quickly equilibrated with interacting soil, and that little additional P was lost into sub-surface flow despite interacting longer with the soil longer than surface runoff. McDowell et al. (2001) used ^{33}P to establish that equilibration times (for P uptake or release) were best estimated by short (< 1 min) extractions for both surface runoff and sub-surface flow. Furthermore, McDowell and Sharpley (2003) established that the additional P leaching into soil solution, outside of this short equilibration period, tended to be small. They hypothesized that this was due to P being protected within aggregates and unlikely to diffuse out of the aggregate in time to influence P concentrations in runoff. The Organic soil contained little Al and Fe oxides to retain P meaning equilibration and P release from reactive surfaces was likely quick. Furthermore, the Organic soil was unstructured and therefore contained little protected P within aggregates.

In contrast, P concentrations in surface runoff from the Brown soil tended to be greater than those in sub-surface flow, especially at high target Olsen P concentrations. This is presumably due to surface application and stratification of P in the soil surface that interacted with surface runoff, but was sorbed by less P-saturated soil at deeper depths in sub-surface flow (e.g. Kleinman et al. 2003). Soil moisture influenced concentrations of P fractions in both surface runoff and subsurface flow. Mean concentrations of FRP, PP and FUP in surface runoff from the dry the Organic soil were on average 22, four and twice as enriched as surface runoff from wet soil. This translated into losses where surface runoff in the dry soil was likely due to hydrophobicity causing infiltration-excess conditions (Osborn et al. 1964). However, in contrast to my hypothesis, the major fraction in both wet and dry soil was FRP, despite infiltration-excess surface runoff being noted as more erosive than saturation-excess surface runoff (Pearce 1976), and the fact that soil organic matter can increases aggregate stability by lowering the wettability and increasing the cohesion of aggregates (Piccolo and Mbagwu 1999; Chenu et al 2000; Mataix-Solera and Doerr 2004), facilitating greater particulate transport.

Table 3.2. Mean pre- and post-runoff extractable soil P concentrations for all treatments. *F*-statistics are given for the comparison of treatment means by soil type, moisture and Olsen P rate, and for interactions between soil type and moisture, and soil type and Olsen P rate.

Treatment	Target Olsen P (mg L^{-1})	--------------- Pre–runoff ---------------				--------------- Post-runoff ---------------			
		WEP (mg L^{-1})	$CaCl_2$-P (mg L^{-1})	Olsen P (mg kg^{-1})	TP (mg kg^{-1})	WEP (mg L^{-1})	$CaCl_2$-P (mg L^{-1})	Olsen P (mg kg^{-1})	TP (mg kg^{-1})
Dry	11	0.14	5.33	13	186	0.11	3.60	10	151
Organic	15	0.41	9.80	15	257	0.28	17.80	11	194
	40	0.74	33.03	30	349	0.46	23.58	15	366
	60	1.04	49.73	40	516	0.85	46.81	32	481
	80	1.47	64.83	55	669	1.27	73.89	53	564
Wet	11	0.11	4.72	8	175	0.10	2.60	7	147
Organic	15	0.28	10.67	9	257	0.25	13.51	10	200
	40	0.62	27.22	23	353	0.49	24.17	18	362
	60	0.88	42.17	30	470	0.79	33.94	23	418
	80	1.15	57.42	41	662	1.00	50.95	40	698
Dry	7	0.10	0.02	7	509	0.10	0.15	7	516
Brown	15	0.13	0.04	14	630	0.08	0.18	11	561
	40	0.14	0.06	19	704	0.11	0.12	16	662
	60	0.16	0.08	23	786	0.13	0.14	25	747
	80	0.16	0.09	30	900	0.13	0.08	30	897
Wet	7	0.10	0.02	7	509	0.08	0.18	8	490
Brown	15	0.11	0.03	13	584	0.11	0.16	10	546
	40	0.13	0.05	19	662	0.09	0.13	15	654
	60	0.13	0.08	22	779	0.09	0.12	19	725
	80	0.15	0.08	28	896	0.11	0.09	26	871
F-statistics									
Soil type		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Moisture		<0.001	0.011	<0.001	0.076	0.002	0.078	<0.001	0.601
Olsen P		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Soil × Moisture		0.002	0.809	<0.001	0.335	0.784	0.056	0.194	0.259
Soil × Olsen P		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Moisture × Olsen P		0.469	0.977	0.113	0.794	0.084	0.746	0.118	0.082
Soil × Moisture × Olsen P		0.138	0.730	0.205	0.366	0.032	0.862	0.066	0.098

As mentioned previously, the Organic soil likely contained few receptive aggregates or Al and Fe oxides that would retain P on soil particles. This means that the Organic soil would likely contain little PP, compared to the Brown soil with a moderate ASC. The low ASC of the Organic soil also meant that the enrichment of P in both surface runoff and sub-surface flow was more pronounced with increasing target Olsen P than in the Brown soil. The enrichment of FRP in surface runoff may have also reflected undissolved P-fertiliser particles, which can enrich surface runoff for a period of 60 days after application (McDowell et al. 2003). However, the risk of direct P fertiliser losses declines exponentially with time such that differences even at high application rates would be difficult to detect, but more importantly, FRP (if used as an indicator of P fertiliser) was only a minor fraction of surface runoff in the wet Brown soil where PP dominated.

3.3.5 Implications for management

This study demonstrates that the magnitude of P losses in subsurface and overland flow from Organic soils is strongly influenced by soil moisture and P fertility. Irrespective of the pathway, both soils exhibited FRP and TP concentrations that were in excess of ANZECC (2000) guidelines for good surface water quality (0.010 and 0.033 mg FRP and TP L^{-1}, respectively), even at low soil Olsen P concentrations. The recent National Policy Statement for Freshwater Management (MfE 2014) stipulates that limits must be enforced by Regional Councils in New Zealand by 2030. One such council - Otago has already adopted the recommendations from Biggs (2000) and ANZECC (2000) to derive limits for farm–scale discharges (0.035-0.045 mg L^{-1}) receiving streams and rivers (0.005-0.026 mg FRP L^{-1}) and lakes (0.005-0.033 mg TP L^{-1}) that minimise algal growth (ORC 2014). While farm-scale limits are greater than those in receiving waters, due to removal processes that occur in runoff, they are still at least 200% greater than those found in surface runoff and subsurface flow in Table 3.2.

It is recommended that soil Olsen P concentration are no greater than the agronomic optimum for pasture production (e.g. 25-40 mg Olsen P L^{-1}) to minimise P losses (McDowell et al. 2003a). While I simulated two very different soil moistures, such conditions are common in the Waituna catchment. For instance, during winter the soil moisture deficit is commonly < 10% (McDowell end Monaghan 2015). Data from this study clearly shows that additional strategies are required if water quality limits are to be achieved and pasture production kept optimal.

Table 3.3. Mean concentrations (mg L^{-1}) of FRP, FUP and PP in surface runoff and sub-surface flow. The *F*-values are given for the comparison of log-transformed means by soil type, moisture, target Olsen P and for the interaction of soil type and moisture, and soil type and target Olsen P.

Treatment	Target Olsen P (mg L^{-1})	--- Surface runoff concentrations ---				--- Subsurface flow concentrations ---			
		FRP	FUP	PP	TP	FRP	FUP	PP	TP
Dry	11	0.62	0.13	0.95	1.38	1.78	0.41	0.91	2.49
Organic	15	8.79	1.58	1.97	12.34	22.24	2.1	1.51	25.85
	40	36.08	8.34	11.73	56.16	45.45	4.22	3.22	52.89
	60	84.77	4.59	20.15	109.51	73.17	3.35	5.89	82.41
	80	183.84	4.27	29.15	217.26	206.69	8.94	6.86	225.9
Wet	11	0.10	0.13	0.11	0.34	2.19	0.11	0.53	2.82
Organic	15	3.40	1.06	1.32	5.77	33.15	1.56	2.48	37.19
	40	4.14	2.88	5.47	11.53	70.57	2.24	9.08	81.88
	60	2.63	2.27	2.86	7.75	134.68	1.88	32.06	168.62
	80	3.56	2.83	2.98	7.49	210.75	19.11	20.37	250.22
Dry	7	-[1]	-	-	-	0.02	0.34	0.72	1.08
Brown	15	0.50	0.23	0.36	1.08	0.07	0.34	0.49	0.90
	40	1.57	0.45	2.61	4.63	0.51	0.46	0.78	1.75
	60	0.13	0.12	0.35	0.53	0.37	0.28	1.24	1.90
	80	-	-	-	-	-	-	-	-
Wet	7	0.27	0.05	0.72	1.04	0.08	0.19	0.65	0.89
Brown	15	0.25	0.14	5.20	5.59	0.13	0.25	0.66	1.04
	40	1.18	0.19	7.22	8.60	0.11	0.40	0.63	1.15
	60	-	-	-	-	0.18	0.41	0.67	1.25
	80	2.29	0.31	8.11	10.71	0.14	0.38	0.87	1.39
F-statistic									
Soil type		**<.001**	**<.001**	0.328	**<.001**	**<.001**	**<.001**	**<.001**	**<.001**
Moisture		**0.001**	0.089	0.717	0.192	**0.013**	0.969	**0.007**	**0.024**
Olsen P		**<.001**	**<.001**	**<.001**	**<.001**	**<.001**	**<.001**	**<.001**	**<.001**
Soil × Moisture		**<.001**	0.146	**<.001**	**<.001**	0.883	0.118	0.139	0.350
Soil × Olsen P		0.065	0.484	0.513	0.189	**<.001**	**<.001**	**<.001**	**<.001**
Moisture × Olsen P		0.608	0.146	0.948	0.579	**0.038**	0.081	0.380	0.191
Soil × Moisture × Olsen P		0.096	0.576	0.446	0.256	**<.001**	0.611	0.207	**0.011**

[1] Data missing as there were insufficient runoff events to make statistical comparisons for that treatment.

There is a strong contrast between Brown and Organic soils as, due to possessing greater mineral content and higher ASC, Brown soils lose much less P. On that basis, strategies to mitigate P losses should be tailored to individual soil types. These strategies will also need to account for different loss pathways. For the Brown soil, strategies that mitigate the erosion of PP in saturation-excess surface runoff include: using low-solubility P fertilisers instead of highly water soluble P fertilisers that could be lost in a surface runoff events soon after application and avoiding or restricting the grazing of saturated paddocks (McDowell and Nash 2012).

Table 3.4. Mean losses (mg) FRP, FUP and PP in surface runoff and sub-surface flow. The *F*-values are given for the comparison of log-transformed means by soil type, moisture, target Olsen P and for the interaction of soil type and moisture, and soil type and target Olsen P.

Treatment	Target Olsen P (mg L^{-1})	----------- Surface runoff losses -----------				------- Subsurface flow losses -------			
		FRP	FUP	PP	TP	FRP	FUP	PP	TP
Dry Organic	11	0.22	0.05	0.27	0.53	3.78	0.90	3.30	7.98
	15	1.97	0.35	0.44	2.76	74.06	7.24	5.24	86.54
	40	29.68	6.84	9.79	46.31	137.06	12.51	10.22	159.79
	60	88.32	5.33	38.26	131.91	228.96	10.35	20.02	259.32
	80	47.69	1.10	7.52	56.32	463.08	20.13	16.34	499.55
Wet Organic	11	0.00	0.00	0.00	0.01	6.25	0.33	1.64	8.22
	15	0.10	0.03	0.04	0.17	98.45	4.77	7.70	110.92
	40	0.21	0.29	0.39	0.89	196.9	6.62	25.03	228.54
	60	0.04	0.01	0.02	0.07	280.79	3.95	67.43	352.17
	80	0.18	0.11	0.12	0.41	381.81	27.61	32.44	441.86
Dry Brown	7	-[1]	-	-	-	0.01	0.02	0.05	0.07
	15	0.05	0.02	0.04	0.11	0.01	0.05	0.06	0.12
	40	0.47	0.14	0.78	1.39	0.12	0.09	0.17	0.39
	60	0.01	0.01	0.03	0.06	0.11	0.09	0.47	0.68
	80	-	-	-	-	-	-	-	-
Wet Brown	7	0.04	0.01	0.16	0.22	0.09	0.23	0.76	1.08
	15	0.29	0.14	6.19	6.62	0.10	0.16	0.43	0.70
	40	0.68	0.06	4.22	4.96	0.04	0.14	0.24	0.43
	60	-	-	-	-	0.11	0.24	0.41	0.77
	80	3.03	0.41	10.74	14.18	0.02	0.07	0.15	0.24
F-statistic									
Soil type		0.117	<0.001	0.485	0.272	<0.001	<0.001	<0.001	<0.001
Moisture		0.003	0.007	0.161	0.022	<0.001	0.007	<0.001	<0.001
Olsen P		<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001
Soil × Moisture		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.265	0.001
Soil × Olsen P		0.215	0.226	0.112	0.040	<0.001	<0.001	<0.001	<0.001
Moisture × Olsen P		0.914	0.010	0.487	0.284	<0.001	0.236	0.581	0.109
Soil × Moisture × Olsen P		0.591	0.237	0.416	0.309	<0.001	0.310	0.078	0.011

[1] Data missing as there were insufficient runoff events to make statistical comparisons for that treatment.

In the Organic soil, drip feeding P via a low water soluble P fertiliser may not decrease P losses compared to highly water soluble P-fertilisers as the low ASC implies that there is little sorptive material for P to bind onto (Simmonds et al. 2015). In addition to poor sorption capacity, strategies for the Organic soil should address P loss by sub-surface flow. McDowell and Norris (2015) showed that surface applying aluminium sulphate (alum) to pasture could decrease the availability (and loss) of FRP in sub-surface flow by a third, while Murphy and Stevens (2010) demonstrated a similar effect on WEP following the incorporation of gypsum ($CaSO_4$) into acid

Cambisols and Gleysols. Once in flow, McDowell et al. (2008) showed that back-filling artificial drainage channels with easily-sourced, non-toxic, P-sorbent material removed 80% of FRP from tile drainage. In open drains, Bryant et al. (2012) showed that ditch filtration using flue gas desulfurization gypsum could decrease mean total dissolved (viz. filtered) P concentrations by around 73%. While the mitigation of P from Organic and Brown soils is possible, the cost of doing so may prohibit the farmer from making a profit on the Organic soil. Therefore, at a catchment scale where the two soils abut one another, a strategy to maintain or increase profitability while decreasing P losses may be to concentrate profitable land uses on the Brown soil accepting that any increase in P losses would be more than offset by not farming the low ASC Organic soil.

3.4 Conclusions

The data confirmed the hypothesis that rainfall applied to a dry Organic soil would cause greater P losses in surface runoff than from a wet soil, due to hydrophobicity. However, due to high hydraulic conductivity and poor ASC, the most important loss pathway for the Organic soil was subsurface flow, wet or dry. Due to poor aggregation and low ASC in the Organic soil, much of the P lost was as FRP and not PP as originally hypothesized. In contrast, a moderate ASC meant that much of the P lost from the Brown soil was as PP in saturation-excess surface runoff irrespective of antecedent moisture conditions. The fact that both runoff processes resulted in environmentally unacceptable P losses at agronomically productive Olsen P concentrations means that additional strategies will be required to reduce any impact on surface water quality. These strategies should focus on PP losses in saturation-excess surface runoff from the Brown soil and FRP losses in sub-surface flow from the Organic soil. Where the two soil types abut one another, reducing catchment losses may be best served by focusing on P losses from the Organic soil.

Chapter 4

Influence of phosphorus fertility and liming on amounts and forms of phosphorus leached from an acid Organic soil.

4.1 Introduction

Organic soils are estimated to cover around 200,000 ha in New Zealand (Gibbs 1980). Many of these have been drained to improve soil aeration and resistance to physical damage from machinery and stock (O'Connor et al. 2001). Following drainage, the next step in the development of many Organic soils for pasture production will be to correct poor nutrient content (Zak et al. 2004); for example, with P fertiliser, and soil acidity with lime.

The quantities and forms of sorbed and precipitated P influence soil P retention and hence susceptibility to loss via surface runoff or subsurface flow (viz. leachate). McDowell and Sharpley (2001) and McDowell and Condron (2004) noted that the potential for P loss in water- and $CaCl_2$-extractable fractions (i.e. P available for loss in surface runoff and subsurface flow, respectively) was related to soil P concentration (Olsen P), but also to ASC which is a measure of a soil's Al and Fe-oxide concentration (Saunders et al. 1965).

Liming increases soil pH, but changes to soil pH can profoundly influence the nature and dynamics of P in the soil. For example, liming modifies the relative solubility and net charge of metal oxides (e.g. Fe and Al) and amorphous minerals (e.g. containing Ca) that can sorb and precipitate P (e.g. Lee et al. 2011). In mineral soils, the solubility maximum for orthophosphate in soil solution is around pH 6.1 (Lindsay 1979). Therefore, increasing or decreasing soil pH to around this level may increase the potential for P loss, especially if the soil has few sorption sites (i.e. a low ASC). There is also some suggestion that liming increases the mineralisation of organic matter (OM) and associated P, often transforming insoluble P into more bioavailable forms (Haynes 1982; Sinclair et al. 1993; Andersson and Nilsson 2001; McDowell and Sharpley 2001). In addition, mineralisation releases low molecular weight aliphatic organic acids (Haynes and Mokolobate 2001) that can reduce P sorption by competing with inorganic P for sorption sites (Gu et al. 1994; Hinsinger 2001). This study therefore investigated the influence of lime and P fertiliser applications on filtered inorganic and organic P losses from a low ASC, acid Organic soil. Due to a very high infiltration rate, surface runoff was deemed unlikely from this soil and losses were measured in leachate from lysimeters. I hypothesised that the quantity and soluble unreactive fraction of P (which includes organic P; Gjettermann et al. 2007) lost from the soils in drainage would increase with increasing pH as organic matter would be mineralised and that losses would be exacerbated when P fertiliser was also applied.

4.2 Materials and Methods

4.2.1 Study site

The Waituna catchment (46° 34’S/168° 36’E) has a surface area of 210 km^2 (Schallenberg et al. 2010) and drains into the Waituna Lagoon and wetland. Soil types range from well-drained Brown soils (USDA Taxonomy, Dystrochrepts; Hewitt 2010) at the northern-end, to poorly-drained acid Organic, Gley and Podzols (USDA Taxonomy, Hemists, Aquepts and Aquods; (USDA Taxonomy, Hemists, Aquepts and Aquods; Hewitt 2010) at the southern-end of the catchment (Wilson 2011). Farming in the Waituna catchment is largely dairying, with operations covering around 80% of pastoral land in the catchment (Risk 2011). Of these dairy farms 25 are situated in the southern portion of the catchment where Organic soils (including Podzols and Gleys with peat-like topsoils) are dominant.

Soil for the trial was taken from a single paddock at the southern-end of the catchment and was classified as an Invercargill peat (acid, mesic Organic soil, New Zealand soil classification; USDA Taxonomy, dysic, mesic Typic Medihemist). This soil had a low extractable P concentration and bulk density, was acidic and had a very low ASC (and oxalate extractable Al and Fe concentrations) (Table 4.1). The paddock had been in production for one year under a forage crop of swede (*Brassica napobrassica* sp.). It had not received fertiliser or lime in the nine months prior to soil collection. Soil was collected from below the plough layer (30 – 60 cm depth) to minimise the chance of sampling soil that had was influenced by fertiliser or lime.

Soil was air-dried, crushed and passed through an 8-mm sieve before being packed into lysimeters at a field bulk density (0.31 g cm^3).

Table 4.1. Selected soil physiochemical characteristics of the unaltered acid mesic Organic soil.

------- Phosphate extracts -------			------------- Soil physiochemical properties -----------					Oxalate extractable	
Olsen P ($mg\ L^{-1}$)	WEP ($mg\ L^{-1}$)	$CaCl_2$-P ($mg\ L^{-1}$)	Bulk density ($g\ cm^3$)	pH	ASC (%)	C (%)	N (%)	Al ($mg\ kg^{-1}$)	Fe ($mg\ kg^{-1}$)
7	0.14	3.14	0.31	4.2	2	37.6	1.0	419.8	180.8

4.2.2 Lysimeter set up and leachate collection

Forty-eight lysimeters were placed in a precipitation and temperature-controlled (25 °C) greenhouse at the AgResearch - Invermay Agricultural Centre, Mosgiel. They were arranged in a randomised block, two-by-eight metre row-column design with additional lysimeters around the outside to reduce the potential for edge effects (Hurlbert 1984). Lysimeters consisted of 6 L polyethylene pots with a nylon mesh (1000 µm) covering a 5-mm hole drilled in the bottom to prevent soil loss and allow drainage along 4-mm tube to 3 L vented bottles. As soils were re-packed and received regular rainfall, edge flow and drying effects were not of concern (Cameron et al. 1992).

Treatments consisted of four replicates of sieved (< 2 mm) single superphosphate (9% P) inputs ranging from a nil or regular maintenance application (0 or 50 kg P ha^{-1} yr^{-1}) to a capital application of 100 or 200 kg P ha^{-1} yr^{-1}, all at three pH values (4.5, 5.5 and 6.5). Manipulations of pH were made using a 1:5 ratio of laboratory grade $Ca(OH)_2$ and $CaCO_3$ (hereafter referred to as lime). Liming rates required to increase soil pH to 4.5, 5.5 and 6.5 were calculated from Lierop (1983). Lime was mixed homogenously through the lysimeters, followed by a three week equilibration period containing three wetting and drying cycles.

Following equilibration, lysimeters were watered with 50 mm of tap water (with an established P concentration lower than 0.005 mg P L^{-1}) every two days until leaching was noted. Ryegrass was sown at a rate of 22 kg ha^{-1} (Young et al. 2010) then lysimeters were watered daily to retain moisture until germination without causing leaching. After two weeks, fortnightly additions of 10 mm of ¼ strength P-deficient Hoagland solution were applied

(Hoagland and Arnon 1950). Three weeks after germination, ryegrass was trimmed to a dry matter residual of 1,500 kg ha^{-1} and repeated at monthly intervals. Three weeks after germination, 40 mm of tap water was applied to lysimeters over a 72 hour period (13.3 mm day^{-1}) using a commercial garden sprinkler system (2 mm full circle micro jet spray fittings) to trigger leaching across all lysimeters. This was followed by three, computer-controlled two-minute daily rainfall cycles over the duration of the experiment, with leachate regularly collected from lysimeters over the 12 month span of the experiment. Precipitation approximated the mean annual rainfall of 1,025 mm recorded from 1975-2011 at a research farm (20 km north of study site).

4.2.3 Analyses

Herbage was trimmed at monthly intervals, dried at 60 °C and weighed to assess the cumulative dry matter yield over the 12 month trial period. Leachate samples were filtered (0.45 µm) immediately following each drainage event and analysed for FRP within 24 h and total filtered P following acid-persulphate digestion (Rowland and Haygarth 1997) within 7 days. Filtered unreactive P was obtained as the difference between TFP and FRP. The P concentration was determined colorimetrically using the method of Watanabe and Olsen (1965), and the quantity of P lost was calculated from the leachate volume and P concentration.

Prior to leaching, a single 25 x 2 cm core was taken from each pot and replaced with moist untreated soil. A soil core was also taken at the end of the trial. Soil cores were oven dried and passed through a 2-mm sieve and then analysed for ASC (Saunders 1965), Olsen P (Olsen et al. 1954), WEP and $CaCl_2$-P (McDowell and Condron 2004). Soil pH was determined by mixing air-dried soil with deionised water at a 1:10 ratio (Hendershot et al. 1993). Bulk density was established as the dry weight of a sample, divided by the volume occupied (Parent and Caron 1993). The amount of Fe and Al (non-crystalline and poorly crystalline forms) in soils was determined using the oxalate-extractable method of McKeague and Day (1966). Soil P fractionation was conducted using the method of Chen et al. (2000).

4.2.4 Statistical analysis

Data was analysed using an ANOVA for two independent variables: soil pH (4.5, 5.5 and 6.5) and fertiliser P rate (0, 50, 100 and 200 kg P ha^{-1}), and their interactions. Data was log-transformed where necessary. The resulting *P*-values are presented in tables and least significant difference at the 5% level is shown for graphs of FRP and FUP; Figures 4.1a and 4.1b. A *t*-test was also conducted to explore differences between extractable P and soil P fractions before and after leaching. All statistical analyses were performed using the statistical package - GenStat version 16 (Payne et al. 2011).

4.3 Results and Discussion

4.3.1 Soil physical and chemical properties

Over the 12 month leaching period there were a number of changes to soil chemical properties (Table 4.2). All soils exhibited a decrease in pH after leaching, such that no difference was noted between mean soil pH for pH 4.5 and 5.5 treatments; however, the pH 6.5 treatment still maintained a greater pH than the other treatments. Soil Olsen P, $CaCl_2$-P and WEP concentrations declined for all pH treatments after leaching with the greatest changes in pH 4.5 and 5.5 treatments. Interestingly, mean pre-leaching Olsen P concentrations for pH 6.5 treatments were less than those of pH 4.5 and 5.5 treatments, suggesting that applied P may have been incorporated into non-bicarbonate extractable pools with the addition of lime. Other studies have noted a decline in Olsen P concentrations coincident with liming; attributing this to enhanced phosphate adsorption from precipitation with Ca (Sorn-Srivichai et al. 1984; Curtin and Syers 2001). The inconsistent pre-leaching Olsen P values for pH 4.5 treatments were most likely because Olsen P tests were conducted outside the optimum pH range for the test (Olsen et al. 1954).

4.3.2 Phosphorus losses in leachate

In keeping with other studies of P loss following the addition of P fertilisers (e.g. Withers et al. 2001), FRP losses in leachate increased with P fertiliser rates for all pH treatments (Figure 4.1a). The lowest cumulative FRP losses were from pH 5.5 and 6.5 treatments, which were generally not different from one another, except at the 100 kg P ha rate where pH 5.5 FRP loss was greater than at pH 6.5. The decreased loss compared to pH 4.5 point to a mitigation effect by the addition of lime. A number of papers have described increased P desorption from soils following the application of lime, citing increases due to: 1) a net increase in the negative charge on soil colloids that limits P sorption (Lindsay 1979); and 2) the mineralisation of soil organic P (Haynes 1982a; Sinclair et al. 1993). However, these data were for mineral soils that contain substantial quantities of Al, Fe and Ca. The acid mesic Organic soil in the present study had a very low ASC (2%; Table 4.1), thus the likelihood that inorganic phosphates are bound to Al or Fe is far less than the likelihood of being bound by Ca (Hsu and Jackson 1960). Indeed, the solubility equilibria of soils limed to pH 5.5 and above indicate that amorphous Ca-phosphates and pure Ca-phosphate such as brushite ($CaHPO_4{\cdot}2H_2O$) may begin to form (Lindsay 1979; Haynes 1982a; Chepkwony et al. 2001; McDowell et al. 2002), and P extracted with NaOH (indicating P associated with Fe and Al oxides) was very low in comparison with other studies (e.g. Chen et al. 2000) and did not change after leaching (Table 4.3).

Similar to my study, Lee et al. (2011) found that increasing soil pH from 5.1 to between 5.5 and 5.8 with $Ca(OH)_2$ significantly reduced total, unreactive and dissolved P concentrations in leachate. This was due to the conversion of WEP fractions into Ca-bound (Ca-P) forms in an Entisol soil – a silt loam soil devoid of Al and Fe oxides. In a Spodosol (pH 4.6) rich in organic matter, but poor in Al or Fe, Olsen and Sommers (1982) noted that applying 1 t ha^{-1} of lime increased soil pH to 7.4 and increased P retention due to the precipitation of Ca-P.

While FRP is immediately bioavailable to plants and algae, the bioavailability of organic P species measured collectively as FUP varies (Toor et al. 2003; McDowell et al. 2008). Filtered unreactive P losses followed a similar pattern to FRP, with mean losses increasing with P application rate and were greatest from pH 4.5 treatments (Figure 4.1b; Perrott and Mansell 1989). However there was no significant difference between FUP losses at pH 5.5 and 6.5 at any P application rate. The proportion of FUP as TFP increased with pH ($P < 0.01$), but was probably due to changes in FRP since FUP only made up – at most, 20% of TFP losses.

Table 4.2. Mean soil pH and P extract concentrations before and after leaching and the P-values (bold if significant) indicating significant changes in means of pH and P extracts by pH, P rates and the interaction of pH by P rates after leaching.

		--------- Before leaching ---------				------------ After leaching ------------			
Soil pH	Fertiliser rate (kg P ha^{-1})	pH	Olsen P (mg L^{-1})	CaCl$_2$-P (mg L^{-1})	WEP (mg L^{-1})	pH	Olsen P (mg L^{-1})	CaCl$_2$-P (mg L^{-1})	WEP (mg L^{-1})
4.5	0	4.7	26	20.0	0.15	3.8	8	0.5	0.09
	50	4.5	58	29.7	0.41	3.8	9	0.9	0.08
	100	4.3	46	55.3	0.73	3.7	13	0.8	0.09
	200	4.5	40	58.8	0.89	3.6	13	1.1	0.09
	Mean	4.5	42	41.0	0.55	3.7	11	0.8	0.09
5.5	0	5.1	14	7.9	0.19	3.9	6	0.9	0.08
	50	4.9	28	21.9	0.33	4.0	9	1.1	0.09
	100	5.0	62	27.8	0.55	3.9	7	1.4	0.10
	200	4.9	92	73.9	1.24	3.9	17	2.8	0.13
	Mean	5.0	49	32.9	0.58	3.9	10	1.6	0.10
6.5	0	6.9	13	3.9	0.16	4.8	5	0.5	0.08
	50	6.7	31	7.7	0.24	4.8	14	0.9	0.08
	100	6.5	38	11.9	0.43	4.8	19	1.3	0.13
	200	6.4	63	29.8	0.66	4.9	28	1.5	0.13
	Mean	6.6	36	13.3	0.37	4.8	17	1.1	0.11
P value									
pH						**<0.001**	**0.013**	**<0.001**	0.093
P rate						0.991	**<0.001**	**<0.001**	0.038
pH × P rate						0.987	0.154	0.516	0.349

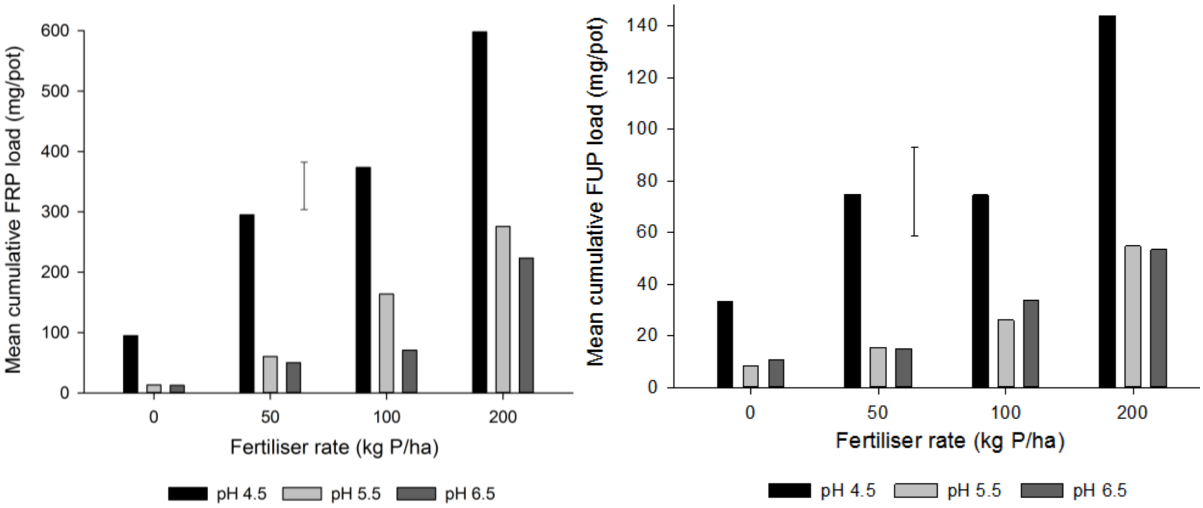

Figure 4.1. a) Mean cumulative FRP and b) FUP load at each fertiliser rate and soil pH. The least significant difference at the $P < 0.05$ level is given for the comparison between all P rates and pH treatments.

Table 4.3. Mean concentrations of inorganic and organic P (mg P kg^{-1}) fractions for soils before, and after leaching at pH 4.5, 5.5 and 6.5 treated with 0, 50, 100 and 200 kg P ha^{-1}. The corresponding *P*-values (bold if significant) are given for the comparison of means by pH and fertiliser rate, and for the interactions of these treatments.

Soil pH	Fertiliser rate (kg P ha^{-1})	---------------------------------- Before leaching P fractions (mg kg^{-1}) ----------------------------------								----------------------------------- After leaching P fractions (mg kg^{-1}) --------------------------------							
		NH_4Cl	$NaHCO_3$-P_i	NaOH-P_i	HCl	$NaHCO_3$-P_o	NaOH-P_o	NaOH-II-P_o	Residual	NH_4Cl	$NaHCO_3$-P_i	NaOH -P_i	HCl	$NaHCO_3$ -P_o	NaOH-P_o	NaOH-II-P_o	Residual
4.5	0	87	37	62	8	27	32	2	4	9	30	98	2	12	45	2	2
	50	227	73	97	11	19	24	2	3	13	28	99	2	12	24	2	2
	100	410	114	78	22	15	24	2	4	12	27	73	3	14	61	3	1
	200	517	135	94	17	29	38	2	5	15	32	93	4	17	43	2	2
5.5	0	75	53	59	15	18	35	1	3	12	26	79	2	16	62	6	2
	50	210	77	71	15	8	19	1	4	15	31	86	2	13	43	2	2
	100	302	101	75	41	20	60	2	3	16	31	86	5	15	27	5	1
	200	505	198	89	45	19	26	2	4	29	35	84	7	14	34	2	1
6.5	0	46	46	59	15	13	30	2	4	13	26	92	3	9	23	2	2
	50	146	101	70	36	18	37	3	4	20	32	79	6	18	47	6	1
	100	254	194	98	64	19	29	2	3	34	42	99	9	14	31	2	2
	200	514	227	131	79	41	42	1	3	42	50	80	17	16	31	3	1
P values																	
pH		**0.009**	**0.004**	0.081	**<0.001**	0.394	0.879	0.821	0.410	**<0.001**	**0.005**	0.530	**<0.001**	0.573	0.325	0.443	0.869
P fertiliser rate		**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.204	0.817	0.676	0.340	**<0.001**	**<0.001**	0.873	**<0.001**	0.634	0.803	0.960	0.271
pH × P fertiliser rate		0.597	0.200	**0.039**	0.834	0.453	0.235	0.061	0.675	0.110	**0.049**	0.284	0.291	0.535	0.197	0.219	0.237

4.3.3 Phosphorus transformations and distribution

Similar to initial soil tests, the quantity of inorganic P (Pi) extracted from soils among different fractions increased with P fertiliser rate before leaching (Table 4.3). The majority of Pi in pre-leachate soils was located in bioavailable (NH_4Cl- and $NaHCO_3$-extractable) forms, due to the low metal-oxide concentration of the soil (Table 4.1). For treatments that received P, *t*-tests indicated the amount of NH_4Cl- and $NaHCO_3$-extractable forms decreased significantly after leaching. For example, decreases in NH_4Cl-Pi compared to pre-leachate concentrations in the 200 kg P ha^{-1} treatments were 97.2%, 94.3% and 91.9% at pH 4.5, 5.5 and 6.5, respectively. The addition of lime increased the proportion of P that was extracted by HCl. Before leaching, pH 6.5 soils extracted 236% and 68% more HCl-extractable P on average than pH 4.5 and 5.5 soils, respectively. The data supports enhanced P retention in the soil due to the formation of sparingly soluble Ca-phosphates (e.g. Haynes 1982b; Naidu et al. 1990; Chepkwony et al. 2001; Lee et al. 2011). Post-leaching, some P was still extractable by HCl in the pH 6.5 soils, but almost none remained in the pH 4.5 or 5.5 soils – commensurate with the acid pH of the soils after leaching (Table 4.2).

My hypothesis also stated that with increasing pH, dissolved organic P losses would increase. Soil fractionation showed there were no significant changes to extractable organic P for pH treatments or P fractions before or after leaching, indicating that net mineralisation did not occur (Table 4.3). There are several potential reasons for this, such as little to no microbial activity or exudation of organic acids by plant roots (Chen et al. 2002). Microbial and plant P requirements are likely to have been met by the large quantities of inorganic P in soil solution and hence there was no need to mineralise organic P for growth (Olander and Vitousek 2000). This was confirmed by the fact that there was no significant differences between P rates and dry matter production (data not shown as a result). The only difference noted was a greater yield in the pH 5.5 and 6.5 treatments compared to pH 4.5 most likely due to the pH range for the optimal growth of ryegrass which sits at between 5.5 and 7.5 (Hannaway et al. 1999). However, the role of organic P could increase as soil fertility increases and more P is present in organic forms (Perrott et al. 1992).

The mass balance presented in Figure 4.2 indicated that there was relatively little variation in soil P fractions between soil pH and fertiliser rates, compared to leachate losses and plant material. This indicates that the added P was either present in poorly-sorbed (and leached) or bioavailable P (incorporated into plant biomass) forms, leaving only original soil P in soil at the end of the trial (Table 4.2). However, it is important to realise that this was a short-term study and with P losses being so high (93, 37 and 24% of the P added [calculated as FRP] at pH 4.5, 5.5 and 6.5, respectively) it is clear that on this low ASC soil, liming to pH 6.5 will still result in substantial P losses in leachate.

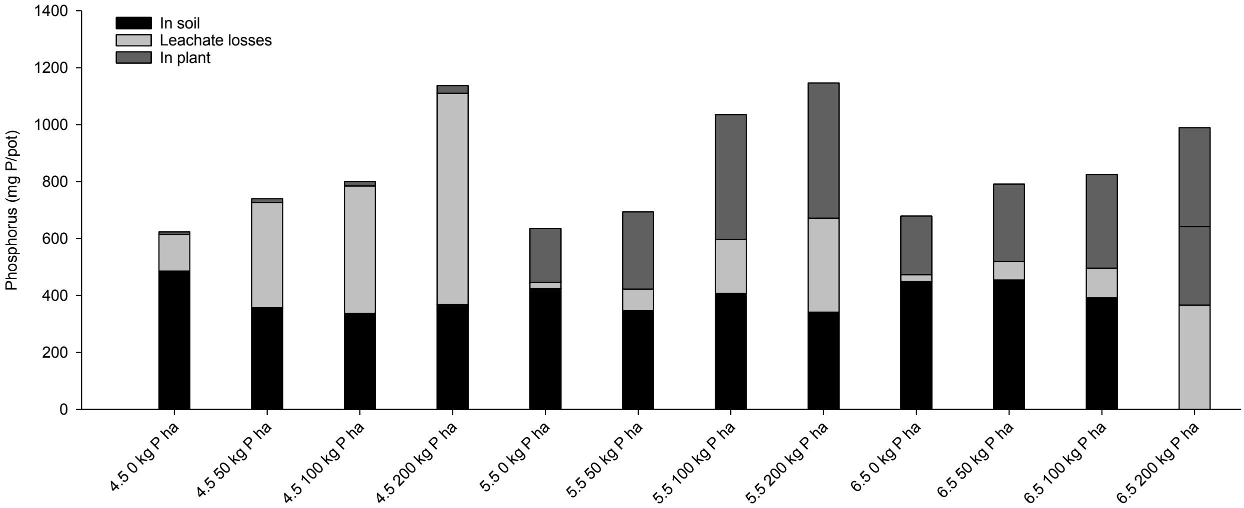

Figure 4.2. Mass balance showing the mean distribution of P at the end of the experiment for each pH treatment and rate. The mean unaccounted P (i.e. difference between soil P + mean rate of added P and the distribution at the trial's end) was 29.2 mg pot-1 ± 64.1.

4.4 Conclusions

Due to the low metal oxide content of the acid mesic Organic soil, applied P was loosely-bound to soil, and therefore mobile. Assuming that in the absence of metal oxides, the addition of lime promoted the formation of insoluble Ca-phosphates, I conclude that P concentrations in leachate subsequently reduced when pH was > 5.5. Phosphorus losses were not enhanced by mineralisation of organic matter, resulting in higher organic P losses as originally hypothesised. However, the magnitude of P losses (51% of P added, on average) in leachate from this low ASC soil, even at pH 6.5, was so great that they represent not only an environmental loss but also a significant economic loss.

Chapter 5

Can low-water solubility phosphorus fertilisers decrease phosphorus leaching loss from an acid peat subsoil?

5.1 Introduction

The risk of surface runoff of P is greatest when water soluble forms of P fertiliser (e.g. SSP) are applied when a surface runoff event is likely to occur (McDowell et al. 2003). This risk can be decreased by using sparingly soluble forms of P fertiliser (e.g. reactive rock phosphate, RPR) that slowly dissolves into soil solution when soil pH is < 6.0 (Bolan et al. 1990; Kanabo and Gilkes 1987; McDowell and Catto 2005). McDowell et al. (2010) assessed the relative P loss from two 12 ha catchments fertilised with either RPR or SSP, and showed that FRP and TP losses were on average 58% and 38% less, respectively, when RPR was applied. However, no data is available for sub-surface losses where interaction with the soil matrix (via Al- and Fe-oxides) is thought to prevent excessive P losses – irrespective of the form of P applied.

Organic soils (peats including Histosols and Hemists in FAO and UDSA Taxonomy, respectively) are estimated to cover between 230 and 450 million hectares (ha) worldwide (Armentano 1980); New Zealand has around 200,000 ha (Gibbs 1980). The majority of New Zealand's Organic soils have been drained, which aside from the agronomic benefits of less waterlogging, improved aeration and resistance to physical damage from machinery and stock, provides an efficient conduit for P to be lost to receiving surface waters where it can enhance eutrophication (O'Connor et al. *2*001; McDowell et al. *2*009). Losses are aided by the fact that many Organic soils poorly sorb or retain P: measured in New Zealand as Al- and Fe-oxides contributing to ASC (Saunders 1965).

Without inputs of lime to maintain soil pH at agronomically viable levels (compared to a mineral soil), the pH of Organic soils can be low. Acidic conditions increase the dissolution rate of RPR. While a combination of high hydraulic conductivity, acidic conditions and low ASC, implies that RPR would be dissolved quickly and potentially lost in subsurface flow, the attenuation and magnitude of leachate losses have not been established. My hypothesis was that there is no environmental benefit in using RPR on these soils compared to SSP, or in other words: dissolved P losses in leachate from acid Organic soils receiving RPR would be similar to those receiving SSP.

5.2 Materials and Methods

5.2.1 Site description

The Waituna catchment (46° 34'S/168° 36'E) has a surface area of 210 km^2 (Schallenberg et al. *2*010) and drains into the Waituna Lagoon and wetland. Soil types range from well-drained Brown soils (USDA Taxonomy, Dystrochrepts; Hewitt 2010) at the northern-end to poorly-drained acid Organic, Gley and Podzols (USDA Taxonomy, Hemists, Aquepts and Aquods, respectively; Hewitt 2010) at the southern-end of the catchment. Pastoral farming covers c. 80% of the Waituna catchment and is dominated by dairying (Stevens and Robertson 2007). Of these dairy farms, around 25 are situated in the southern portion of the catchment where Organic soils (including Podzols and Gleys with peat-like topsoils) are dominant.

Soil for the trial originated from a single location at the southern-end of the catchment and was classified as an Invercargill peat (acid, mesic Organic soil, New Zealand soil classification; USDA Taxonomy, dysic, mesic Typic Medihemist). The soils had low extractable P concentrations and bulk density, were acidic and had very low ASC (and oxalate extractable Al and Fe concentrations) (Table 5.1). The area had been developed from native swamp and had been in production for one year under a forage crop of swede. It had not received fertiliser or lime in the 9 months prior to soil collection. Soil was collected from below the plough layer (30 – 60 cm depth) to minimise the chance of sampling soil that had received fertiliser. Soil was air-dried, crushed and passed through an 8-mm sieve before being packed into lysimeters at a field bulk density (0.31 g cm^3).

Table 5.1. Selected soil physicochemical characteristics of the control acid mesic Organic soil.

Phosphorus extracts			---- Soil physiochemical properties ----					Oxalate extractable	
Olsen P (mg L^{-1})	WEP (mg L^{-1})	$CaCl_2$-P (mg L^{-1})	Bulk density (g cm^3)	pH	ASC (%)	C (g kg^{-1})	N (g kg^{-1})	Al (mg kg^{-1})	Fe (mg kg^{-1})
7.0	0.14	3.14	0.31	4.2	2.0	376	10	420	181

5.2.2 Lysimeter set up and collection

Eighty-four lysimeters were placed in a light and temperature-controlled greenhouse at the Invermay Agricultural Centre, Mosgiel, New Zealand. They were arranged in a randomised block, two-by-eight metre row-column design with additional lysimeters around the outside to reduce the potential for pseudoreplication and edge effects (Hurlbert 1984). Lysimeters consisted of 6 L polyethylene pots with a nylon mesh (1000 µm) covering a 5 mm hole drilled in the bottom to prevent soil loss and allow drainage along 4 mm tube to 3 L vented bottles. As soils were re-packed and received regular rainfall, edge flow and drying effects were not of concern (Cameron et al. *1*992).

Treatments consisted of four replicates of four sieved (< 2 mm) SSP (9% P) or RPR (13% P) inputs ranging from a nil or regular maintenance application (0 or 50 kg P ha^{-1} yr^{-1}) to a capital application of 100 or 200 kg P ha^{-1} yr^{-1}, all at three pH values (4.5, 5.5 and 6.5). Manipulations of pH were made using a 1:5 ratio of laboratory grade $Ca(OH)_2$ and $CaCO_3$ (hereafter referred to as lime). Liming rates required to increase soil pH to 4.5, 5.5 and 6.5 were calculated from Lierop (1983). Lime was mixed homogenously throughout the soil in the lysimeters, followed by a six week equilibration period containing three wetting and drying cycles.

Lysimeters were initially watered with 50 mm of tap water (with an established P concentration lower than 0.005 mg P L^{-1}) every two days until leaching was noted. Ryegrass was sown at a rate of 22 kg ha^{-1} (Young et al. *2*010) then lysimeters were watered daily to retain moisture until germination without causing leaching. After two weeks, fortnightly additions of 10 mm of P-deficient ¼ strength Hoagland solution were applied (Hoagland and Arnon 1950). Three weeks after germination, ryegrass was trimmed to a dry matter residual of 1,500 kg ha^{-1} and repeated at monthly intervals. Shoot material was bulked together within each lysimeter. Three weeks after germination, 40 mm of tap water was applied to lysimeters over a 72 hour period (13.3 mm day^{-1}) using a commercial garden sprinkler system (2 mm full circle micro jet spray fittings) to trigger drainage across all lysimeters. This was followed by three, computer-controlled two-minute daily rainfall cycles over the duration of the experiment, with leachate regularly collected from lysimeters over the 12 month span of the experiment. Precipitation approximated the mean annual rainfall of 1,025 mm recorded from 1975-2011 at a research farm near the Waituna catchment.

5.2.3 Analyses

Leachate samples were filtered (0.45 µm) immediately following collection and analysed for FRP within 24 h and FUP following acid-persulphate digestion (Rowland and Haygarth 1997) within 7 days (FUP estimated as the difference between TFP and FUP). The P concentration was determined colorimetrically using the method of Watanabe and Olsen (1965), and P loss (load) was determined by combining concentration and leachate volume data for each lysimeter.

Plant matter was harvested at monthly intervals, dried at 60 °C and weighed to determine the cumulative dry matter yield over the 12 month trial period. At the end of the trial pasture roots were washed from each lysimeter, dried at 60 °C, weighed and bulked with the corresponding shoot material. Separate sub-samples (1 g) of shoot and root material from each lysimeter was ground in a stainless steel mill and digested using HNO_3 and $HClO_4$ mixed in 4 to 1 ratio (Crosland et al. 1995).

At the start of the trial, a single 25 x 2 cm core was taken from each pot and replaced with new soil from each treatment. A similar core was also taken at the end of the trial. Soil cores were oven dried and passed through a 2 mm sieve prior to analysis of ASC (Saunders 1965) and bicarbonate-extractable Olsen P (Olsen et al. *1*954). Water extractable P (McDowell and Condron 2004) and $CaCl_2$-P were also determined as good indicators of the potential for P loss via surface runoff and subsurface flow, respectively (McDowell and Sharpley 2001). Soil pH was determined by mixing air-dried soil with deionised water at a 1:10 ratio (Hendershot et al. 1993). An estimate of bulk density was established as the dry weight of a sample, divided by the volume occupied (Parent and Caron 1993). The amount of Fe and Al (non-crystalline and poorly crystalline forms) in soils was determined using the oxalate-extractable method of McKeague and Day (1966). Soil P fractionation was conducted using the method of Chen et al. (2000).

The fate of the fertiliser-P applied was apportioned into soil, plant and leachate via a mass balance of the product of total P concentration and weight (or volume) for each of the constituent pools. Existing soil P was taken into account by subtracting the mass of total P for unfertilised soil.

5.2.4 Statistical analysis

Data were analysed using an ANOVA fitting factors for fertiliser type (SSP and RPR, plus no fertiliser), soil pH (4.5, 5.5 and 6.5) and fertiliser P rate (50, 100 and 200 kg P ha^{-1}), and their interactions. All data required log-transformation except cumulative dry matter. Of the possible interactions, only those for fertiliser type by pH were significant. The significance of this interaction and the magnitude of difference are shown in tables as the ratio of SSP to RPR. All statistical analyses were performed using the statistical package - GenStat version 16 (Payne et al. 2011).

5.3 Results and Discussion

5.3.1 Leachate analyses

Data for mean losses of FRP and FUP are given in Table 5.2. When taken as an average of all P rates, FRP and FUP losses from pH 4.5 SSP-treated soils were 165% and 211% greater than at pH 5.5, and 281% and 189% greater than at pH 6.5. In comparison, FRP and FUP losses from pH 4.5 RPR-treated soils were 158% and 185% greater than pH 5.5 treatments, and 585% and

326% greater than 6.5 treatments. Given all lysimeters received the same irrigation rate, leaching losses would be a function of how available the applied- P was and uptake either by the soil or pasture. A number of studies (Haynes 1982; Naidu et al. 1990; Chepkwony et al. 2001; Lee et al. 2011) have found that liming soils to pH 5.5 and above increases P retention/sorption due to the formation of Ca-phosphates in soils with low sorption capacity, while the application of lime can reduce RPR dissolution (He et al. 1996).

Table 5.2. Mean FRP and FUP losses (mg P pot^{-1}) in leachate from soils at pH 4.5, 5.5 and 6.5 treated with RPR or SSP. The standard error of the difference (SED) and P-values relate to a comparison of means for P fractions between fertiliser treatments at each pH along with the relative strength of difference given as the ratio of means for SSP to RPR.

		---------- Treatment ----------					
	pH	Control	RPR	SSP	SED	P	Ratio (S/R)
FRP	4.5	94.1	307.4	405.6	27.6	0.002	1.3
	5.5	12.2	126.6	145.0	23.5	0.440	1.1
	6.5	12.3	34.2	112.5	21.9	0.002	3.3
FUP	4.5	35.9	75.1	95.9	17.5	0.247	1.3
	5.5	8.3	27.4	28.5	4.0	0.785	1.0
	6.5	11.1	16.1	30.9	2.9	<.001	1.9

There were differences between FRP and FUP losses as a function of fertiliser type, but only at certain pH levels (Table 5.2). In general, there was little difference (expressed as the ratio of losses from SSP to RPR) in mean FRP and FUP losses between the two fertiliser types at pH 4.5 and 5.5. However, FRP loss from SSP treated soils at pH 6.5 was three-times that lost from RPR amended soils. Although, there was more FRP lost from the SSP compared to RPR soil at pH 4.5, the difference was not strong (ratio = 1.3; Table 5.2). Interestingly, FUP losses were greater from SSP than RPR treated soils at pH 6.5, suggesting increased loss of organic P. However, there was little change in soil organic P over the duration of the experiment (see next section). It is possible that the acidifying nature of SSP (e.g. Horsnell 1985), especially at high application rates, may have solubilised a small amount of organic P, detectable in leachate, but not detected as a change in soil organic P.

5.3.2 Soil P fractionation

Before leaching the addition of fertiliser P increased, on average, the concentration of all extractable inorganic P pools (NH_4Cl, HCO_3, NaOH, and HCl) compared to unfertilised soil, but not concentrations of extractable organic P. It is well established that adding fertiliser enriches inorganic P in readily bioavilable pools (e.g. Rowarth et al. *1*992) until processed within the soil and redistributed into more recalcitrant pools (McDowell et al. *2*010; Chen et al. *2*000). It is also known that the distribution and magnitude of P in different pools can be influenced by the form of P applied and its water solubility. For instance, Metherell et al. (1997) compared the accumulation of P fractions in organic and inorganic soil pools following 17 years of applying Sechura phosphate rock (Sechura PR) and SSP. They noted increases in HCO_3 and NaOH pools were similar for the two fertiliser types, while the sparingly water-soluble Sechura PR treatment still contained significant quantities of undissolved PR extractable by HCl. In my study, differences in inorganic extractable P concentrations between RPR and SSP-treated soils were only noted at pH 6.5 (Table 5.3).

Among P fractions, both treatments contained most P in labile (NH_4Cl- and $NaHCO_3$-extractable) over more recalcitrant NaOH- and HCl-extractable forms (Table 5.3). Of the two most labile fractions, NH_4Cl-extractable P was much greater, probably reflecting the absence of Fe and Al oxides in the Organic soil as indicated by its low ASC (Table 5.1). In mineral soils P fractions are dominated by $NaHCO_3$- and NaOH-extractable forms due to a much greater concentration of Al and Fe oxides (Chen et al. *2*000; Condron and Newman 2011). It is also worth noting that whereas fertiliser P accumulated in NH_4Cl-, $NaHCO_3$-, and NaOH-extractable fractions in SSP-treated soils, soils receiving RPR had more P in the HCl- and, recalcitrant NaOH-II-extractable pools (SSP to RPR ratio of 0.3 and 0.1, respectively). The enrichment of the HCl-extractable P has been attributed to the formation of Ca-phosphates (e.g. Boruvka and Rechcigl 2003; Lee et al. *2*011). However, the Organic soil contained little Ca. Some was added as $CaCO_3$ and with the fertilisers, but as HCl-extractable P was not enriched in the SSP treated (and limed) soils, the enrichment of HCl-extractable P in RPR treated soils is likely to represent undissolved RPR (i.e. apatite).

After leaching, total soil P had significantly decreased (Table 5.4). Among P fractions, all had decreased on average except for NaOH-extractable P which was similar across treatments, suggesting this pool was not as strongly influenced by P fertiliser additions. Of more importance is that differences between fertiliser types after leaching, while still significant in pH 6.5 soils (Table 5.4), had decreased e.g. from 2.4 and 2.5 in the NH_4Cl- and HCO_3-extractable P pools to 1.5 and 1.3, respectively. This reflects a total decrease in both fertiliser treatments but more from the SSP treated soil at pH 6.5. The ratio for SSP to RPR extractable by HCl at pH 6.5 changed relatively little (from 0.3 before leaching to 0.4 afterwards), but it too was greatly depleted by leaching or plant uptake.

Table 5.3. Mean concentrations of P fractions (mg P kg^{-1}) extracted from soils at pH 4.5, 5.5 and 6.5 and treated with RPR or SSP before leaching. The standard error of the difference (SED) and P-values relate to a comparison of means for P fractions between fertiliser treatments at each pH along with the relative strength of difference given as the ratio of means for SSP to RPR.

				Treatment				
	Target pH	Actual pH	**Control**	**RPR**	**SSP**	SED	P	Ratio (S/R)
NH_4Cl	4.5		82.2	404.9	374.2	58.5	0.605	0.9
	5.5		98.6	411.3	379.3	64.2	0.620	0.9
	6.5		45.3	118.5	283.2	37.7	**<.001**	2.4
HCO_3-Pi	4.5		37.9	95.0	107.4	11.5	0.298	1.1
	5.5		53.3	101.8	116.4	11.2	0.210	1.1
	6.5		47.3	68.7	172.7	20.3	**<.001**	2.5
NaOH-Pi	4.5		63.9	79.1	89.6	6.1	0.103	1.1
	5.5		58.7	75.9	78.1	4.9	0.658	1.0
	6.5		58.3	72.0	97.9	8.0	**0.004**	1.4
HCl	4.5		8.4	12.1	16.2	2.5	0.107	1.3
	5.5		17.8	41.7	33.1	11.4	0.451	0.8
	6.5		17.3	179.9	56.4	28.3	**<.001**	0.3
NaOH-II-Pi	4.5		1.0	1.6	2.3	1.0	0.503	1.4
	5.5		2.1	3.5	4.0	1.8	0.798	1.1
	6.5		1.1	33.0	4.7	2.2	**<.001**	0.1
Residual	4.5		4.3	4.8	4.2	0.6	0.318	0.9
	5.5		3.6	4.0	3.7	0.6	0.713	0.9
	6.5		4.6	3.5	3.3	0.6	0.738	0.9
Organic P	4.5		75.8	54.2	57.6	15.3	0.454	1.1
	5.5		141.7	61.1	161.5	67.6	0.386	2.6
	6.5		63.5	64.2	77.8	29.5	0.621	1.2
Total P	4.5		261.1	650.0	642.9	59.0	0.907	1.0
	5.5		290.7	691.1	664.6	72.4	0.718	1.0
	6.5		220.4	559.1	674.1	75.6	0.143	1.2

Table 5.4. Mean concentrations of P fractions (mg P kg^{-1}) extracted from soils at pH 4.5, 5.5 and 6.5 and treated with RPR or SSP after leaching. The standard error of the difference (SED) and P-values relate to a comparison of means for P fractions between fertiliser treatments at each pH along with the relative strength of difference given as the ratio of means for SSP to RPR.

			---------------- Treatment ---------------				
	pH	Control	RPR	Super	SED	P	Ratio (S/R)
NH_4Cl	4.5	9.5	17.0	13.4	2.1	0.099	0.8
	5.5	12.4	30.4	19.6	4.0	**0.014**	0.6
	6.5	13.3	20.9	31.4	4.2	**0.021**	1.5
HCO_3-Pi	4.5	29.8	30.6	29.4	1.8	0.472	1.0
	5.5	26.0	33.9	32.0	2.5	0.463	0.9
	6.5	26.2	31.8	40.8	2.7	**0.003**	1.3
NaOH-Pi	4.5	99.6	76.8	87.3	6.1	0.103	1.1
	5.5	80.8	84.0	85.4	7.2	0.842	1.0
	6.5	94.9	84.6	85.3	7.3	0.925	1.0
HCl	4.5	1.9	2.3	2.9	0.3	0.100	1.2
	5.5	2.2	3.7	4.7	0.8	0.245	1.3
	6.5	4.6	33.7	12.5	7.3	**0.009**	0.4
NaOH-II-Pi	4.5	1.1	1.2	1.2	0.3	0.907	1.0
	5.5	1.9	1.6	1.5	0.4	0.799	0.9
	6.5	2.1	7.8	3.0	1.3	**<.001**	0.4
Residual	4.5	1.9	1.9	1.7	0.4	0.550	0.9
	5.5	2.4	1.8	1.6	0.5	0.646	0.9
	6.5	2.5	1.9	1.4	0.5	0.361	0.8
Organic P	4.5	76.0	48.1	67.6	16.2	0.464	1.4
	5.5	101.7	57.8	54.6	15.7	0.749	0.9
	6.5	37.0	66.8	64.5	24.4	0.677	1.0
Total P	4.5	203.0	181.5	200.6	10.7	0.086	1.1
	5.5	208.3	212.9	196.9	13.4	0.249	0.9
	6.5	174.2	243.6	231.5	18.1	0.511	1.0

5.3.3 Plant production

Soil pH influenced ($P<0.001$, SED = 3.1 mg pot^{-1}) dry matter yield, with little growth at pH 4.5 (10.5 mg pot^{-1}) compared to pH 5.5 (58.4 mg pot^{-1}) and 6.5 (67.9 mg pot^{-1}). The pH 4.5 treatment was well outside the range tolerated by ryegrass of 5.1 to 8.4, and certainly the range for optimal growth at pH 5.5 to 7.5 (Hannaway et al. *1*999). There were not other significant differences between treatments.

5.3.4 Management

Figure 5.1 shows the distribution of P in the various pools at the end of the trial. As soil pH increased and associated plant growth increased, the loss of P by leaching decreased. The major differences between treatments of differing pH and fertiliser type can largely be explained by the quantities of P in plant biomass and leachate losses. The added P was either lost from poorly-sorbed soil (i.e. leached) or was bioavailable P (taken up in biomass), leaving only native soil P at the end of the trial.

The mean costs of using RPR or SSP at a given pH level on an acid Organic soil are given in Table 5.5 on a per hectare basis. These were calculated using the annual leaching losses in Table 5.2, the diameter of the lysimeters and scaled up to a hectare. Differences in costs reflect those in Table 5.2, with significant differences between fertiliser types only evident at pH 6.5. While it is common for Organic soils to be maintained at a pH of 5.0-5.5 (Roberts and Morton 2009) to optimise yield, the added cost of liming to > 5.5 will be compensated for by reduced P losses. Therefore, there are economic and environmental benefits to using RPR as opposed to SSP on an acid Organic soil that is limed to pH 6.5.

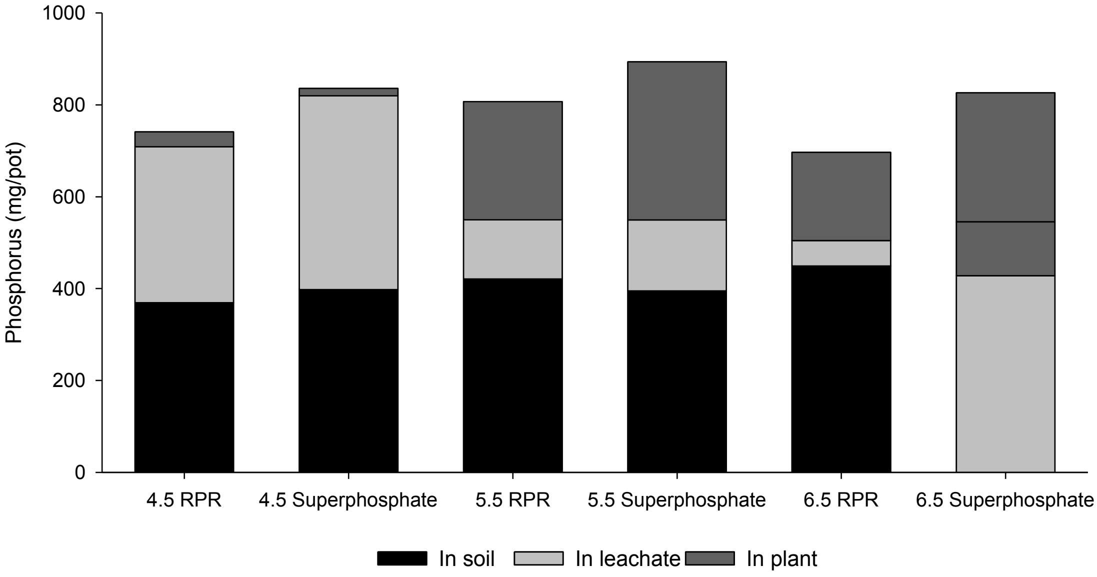

Figure 5.1. Mass balance showing the mean distribution of P at the end of the experiment across each fertiliser type by pH treatment. The mean unaccounted P (i.e. difference between soil P + mean rate of added P and the distribution of P at the trial) was 18.8 mg pot^{-1} ± 52.8.

Table 5.5. Cost of P leached from soils at pH 4.5, 5.5 and 6.5 for soils treated with RPR or SSP – averaged across all P rates. Loads of FRP plus FUP were adjusted to kg P ha^{-1} and costs calculated using a P concentration and cost of 9% and \$3.51 kg P^{-1} for SSP, while the respective P concentration and cost for RPR were 13% and \$2.30 kg P^{-1}.

Soil pH	Fertiliser type	Mean cost of P leached (\$ ha^{-1})[1]
4.5	RPR	\$193
	SSP	\$374
5.5	RPR	\$81
	SSP	\$153
6.5	RPR	\$31
	SSP	\$109

[1] The mean cost of RPR and SSP applied when averaged across all pH and fertiliser rates was \$102 ha^{-1} and \$212 ha^{-1}, respectively.

5.4 Conclusions

At a soil pH of 4.5 and 5.5 the application of RPR to an Organic soil resulted in FRP losses in leachate to a similar extent to those of SSP. However, at pH 6.5, FRP losses from RPR were significantly less than SSP. Soil fractionation analysis showed that the quantities of extractable P were influenced by the fertiliser applied. Pools of loosely-bound and bioavailable inorganic P were greatly enriched by SSP applications. The same occurred for those soils receiving RPR, with the exception that HCl-extractable P was also enriched. All of these pools decreased significantly over the trial period, but still exhibited differences at pH 6.5. These data suggest that there are both agronomic and environmental benefits to using RPR over SSP, when an acid Organic soils soil is limed to pH 6.5.

Chapter 6

The potential for the use of Lotus as a replacement for clover or ryegrass, on an acid Organic soil

6.1 Introduction

New Zealand acid mesic Organic soils are most common in wetlands, or under forest-produced acid litter in areas of high precipitation (Hewitt 2010). These moisture- and carbon-rich environments create conditions that constrain pastoral production, including low soil pH, poor P retention, and a high and variable water table (Guérin et al. 2011). In order to maximise production of pastoral species like ryegrass, Organic soils initially require significant development, including drainage and applications of fertiliser and lime to increase soil P and pH. However, drainage can increase the aeration of Organic soils, which increases microbial mineralisation of organic P and providing a conduit for the rapid movement of P to adjacent surface waters (Schipper and McLeod 2002). The addition of Ca has been shown to increase (and at times decrease) P solubility (Haynes 1982) and hence availability to plants, but also drainage. Compared to more mineral soils, concentrations of Al and Fe metal oxides tend to be poor in Organic soils, resulting in poor P retention (Robson et al. 2011). Hence, the combination of poor P retention, lime and drainage may result in a large proportion of P that is added as fertiliser being at risk of loss in surface runoff or subsurface flow.

Some of these issues could be addressed by opting for a pastoral species that is tolerant of low pH, soil P, and high soil moisture, yet is able to produce good quantities of quality dry matter. Lotus is able to fix nitrogen to soils, reducing N fertiliser requirements, favours low pH soils (approximately 4.7), is shallow rooting, is tolerant of low soil P concentrations and assimilates P quickly (Sheath 1981): *Lotus corniculatus* also produces less methane in sheep (mean = 11.5 g kg^{-1} DMI) in comparison to ryegrass-white clover pasture (mean = 25.7 g kg^{-1} DMI) and lucerne (mean = 20.6 g kg^{-1} DMI) (Waghorn et al. 2002). However, there are difficulties associated with some legumes (e.g. *Lotus* spp.) in that they require a long period of establishment and, in soils of higher fertility, competitive exclusion by other vegetation can limit their potential use as a pastoral vegetation (Lowther et al. 2012). Lotus dry matter production and plant density declines with time under dairying, but this could be slowed using infrequent grazing, which also slows the ingression of weeds (Minneé et al. 2007).

The objective of this paper was to determine productivity (as dry matter yield) and losses (as P in leachate) from lysimeters containing an Organic soil, and monocultures of ryegrass, greater lotus, or white clover, over a pH range of 4.5 to 6.5, with SSP at rates ranging from zero to capital inputs. The hypothesis was that productivity and P losses are better in a lotus-based pasture at low pH and soil P concentration than a clover or ryegrass-based pasture. If true, this could open up the potential for lotus to be used as an alternative pasture species on poorly-developed marginal soils, as a means to reduce the risk of P loss and environmental impacts.

6.2 Materials and Methods

6.2.1 Study site

Study site and soil data are as outlined in chapters 5 and 6.

6.2.2 Lysimeter set up and collection

One hundred and fourty-four lysimeters were placed in a light and temperature-controlled greenhouse at the AgResearch - Invermay Agricultural Centre, Mosgiel. They were arranged in a randomised block, two-by-eight metre row-column design with additional lysimeters around the outside to reduce the potential for pseudoreplication and edge effects (Hurlbert 1984). Lysimeters consisted of 6 L polyethylene pots with a nylon mesh (1000 µm) covering a 5 mm hole drilled in the bottom to prevent soil loss and allow drainage along 4 mm tube to 3 L vented bottles.

Treatments consisted of three pasture species; perennial ryegrass, greater lotus, and white clover. Each species had four replicates of four sieved (< 2 mm) SSP (9% P) inputs of 0, 50, l00 or 200 kg P ha^{-1}, all at three pH values (4.5, 5.5 and 6.5). Manipulations of pH were made using a 1:5 ratio of laboratory grade $Ca(OH)_2$ and $CaCO_3$ (hereafter referred to as lime). Liming rates required to increase soil pH to 4.5, 5.5 and 6.5 were calculated from Lierop (1983). Lime was mixed homogenously through the lysimeters, followed by a 3 week equilibration period containing three wetting and drying cycles.

Lysimeters were initially watered with 50 mm of tap water (with an established P concentration lower than 0.005 mg P L^{-1}) every two days until leaching was noted. Ryegrass was sown at a rate of 22 kg ha^{-1} (Young et al. 2010) and lotus and white clover at 5 kg ha^{-1} (Charlton and Brock 1980) then lysimeters were watered daily to retain moisture until germination without causing leaching. After two weeks, fortnightly additions of 10 mm of ¼ strength P-deficient Hoagland solution began (Hoagland and Arnon 1950). Germination was interrupted by an 11 day failure in the watering system that coincided with an infestation of fungus gnat (*Mycetophilidae*). This resulted in the destruction of all recently established lotus and clover seedlings. Ryegrass was not affected, and as other concurrently run trials shared ryegrass treatments with this trial, the decision was made to allow ryegrass to grow while new lotus and clover were established. Ongoing attempts were made to eradicate the infestation and had been successful by March 2014. Three weeks after the germination of ryegrass, 40 mm of tap water was applied to lysimeters over a 72 hour period (13.3 mm day^{-1}) using a commercial garden sprinkler system (2 mm full circle micro jet spray fittings) to trigger leaching across all lysimeters, and plants were trimmed to a dry matter residual of 1,500 kg ha^{-1} which was repeated at monthly intervals. This was followed by three, computer-controlled two-minute daily rainfall cycles over the duration of the experiment, with leachate regularly collected from lysimeters over the span of the experiment. Precipitation approximated the mean annual rainfall of 1,025 mm recorded from 1975-2011 at a research farm 20 km north of study site.

Plant matter was harvested at monthly intervals, dried at 60 °C and weighed to assess the cumulative dry matter yield over the 5 month trial period. Leachate samples were filtered (0.45 µm) immediately following each leachate event and analysed for FRP within 24 h and FUP following acid-persulphate digestion (Rowland and Haygarth 1997) within 7 days. The P concentration was determined colorimetrically using the method of Watanabe and Olsen (1965).

Prior to commencement, a single 25 x 2 cm core was taken from each pot and replaced by moist untreated soil. A soil core was also taken at the end of the trial. Soil cores were oven dried and passed through a 2 mm sieve prior to analysis of ASC (Saunders 1965) and Olsen P (Olsen et al. 1954). Water-extractable P (McDowell and Condron 2004) and $CaCl_2$-P were also determined as these have been shown to be good indicators of the potential for P loss via surface runoff and subsurface flow, respectively (McDowell and Sharpley 2001). Soil pH was determined by mixing air-dried soil with deionised water at a 1:10 ratio (Hendershot et al. 1993). Bulk density was established as the dry weight of a sample, divided by the volume occupied (Parent and Caron 1993). The amount of Fe and Al (non-crystalline and poorly crystalline forms) in soils was determined using the oxalate-extractable method of McKeague and Day (1966). Soil P fractionation was conducted using the method of Chen et al. (2000).

6.2.3 Statistical analysis

Data from the 12 month trial was truncated to the last five months when lotus and clover were established. This meant that some P had already been leached. To account for this, treatments were compared as a percentage change from their starting point at germination (i.e. starting from 100% soil P content). This was analysed using an ANOVA for three fixed factors: species (lotus, ryegrass and clover), soil pH (4.5, 5.5 and 6.5) and fertiliser P rate (0, 50, 100 and 200 kg P ha^{-1}), and their interactions. The resulting *P*-values are presented in tables and least significant difference at the 5% level is shown in graphs. All statistical analyses were performed using the statistical package Genstat - version 16 (Payne et al. 2011).

6.3 Results and Discussion

6.3.1 Soil physical and chemical properties

Prior to leaching, there were no significant differences between plant species for mean pH or extractable P at any pH level (Table 6.1). Differences in extractable P and soil pH occurred as expected due to the addition of fertiliser-P and lime, respectively. After leaching, soil pH was still different among treatments, but the overall mean soil pH had decreased compared to that before leaching. This was most likely due to the dissolution of applied lime and its removal into leachate (e.g. Nye and Ameloko 1987; Gunn et al. 2001). There was some suggestion of an enrichment of $CaCl_2$-P in the clover treatment with P additions compared to ryegrass or lotus. There were no other significant effects observed.

6.3.2 Change in phosphorus over time

An objective of this trial was to determine whether P losses could be reduced under a monoculture of lotus, compared to clover or ryegrass. This was evaluated from the percentage decline of FRP in leachate over 5 months (Table 6.2). Data from ANOVA showed that the percentage of FRP decline was only affected by pH for all species, and the least change in FRP was from pH 6.5 treatments. This is most likely because calcium applied to the soil as lime increased P adsorption as Ca-phosphates, reducing extractable P fractions (i.e. WEP; Lee et al. 2011) and increasing P retention (Olsen and Sommers 1982). These results indicate that the proportion of FRP released from soils was not influenced by plant type.

Table 6.1. Mean pre- and post-leaching soil pH and P extract concentrations for clover (C), lotus (L) and ryegrass (R) treatments, and the *P* values indicating significant post-leaching changes between means by treatments of pH, P rates and species, and the interactions of these treatments.

Soil pH	Fertiliser rate (kg P ha^{-1})	Pre-leaching												Post-leaching											
		pH			Olsen P			CaCl$_2$-P			WEP			pH			Olsen P			CaCl$_2$-P			WEP		
		C	L	R	C	L	R	C	L	R	C	L	R	C	L	R	C	L	R	C	L	R	C	L	R
4.5	0	4.8	4.7	4.7	24	28	26	22.2	6.0	20.0	9.6	10.1	9.1	3.7	3.6	3.8	9	8	8	0.6	0.7	0.5	4.2	5.2	5.6
	50	4.5	4.5	4.5	41	48	58	20.6	24.5	29.7	25.0	23.5	24.5	4.0	3.9	4.0	11	12	9	1.3	0.7	0.9	5.7	5.0	4.9
	100	4.4	4.4	4.3	41	40	45	65.3	46.2	55.3	57.2	40.9	43.9	4.0	3.8	4.0	8	12	13	0.8	0.9	0.8	4.8	4.8	5.5
	200	4.6	4.4	4.5	49	45	40	48.4	58.3	58.8	51.6	55.2	53.1	3.9	3.9	3.9	13	11	13	2.5	1.0	1.1	5.3	5.2	5.5
	Mean	**4.6**	**4.5**	**4.5**	**39**	**40**	**42**	**39.1**	**33.8**	**40.9**	**35.9**	**32.4**	**32.7**	**3.9**	**3.8**	**3.9**	**10**	**11**	**11**	**1.3**	**0.8**	**0.8**	**5.0**	**5.1**	**5.4**
5.5	0	5.2	5.3	5.1	11	17	14	4.9	21.5	7.9	9.6	7.6	11.7	3.8	3.8	3.5	8	7	6	0.7	1.0	0.9	5.4	6.1	4.8
	50	5.8	5.2	4.9	26	28	28	17.6	21.7	21.9	15.3	22.9	19.9	3.9	3.9	3.9	8	9	9	1.2	0.9	1.1	5.3	3.7	5.2
	100	5.2	5.0	5.0	30	43	62	30.6	29.7	27.8	30.6	32.7	33.2	4.8	4.9	4.8	15	9	7	2.8	0.8	1.4	5.4	7.1	5.9
	200	4.9	4.8	4.9	66	85	92	54.4	64.4	73.9	51.1	58.8	74.1	4.8	4.8	5.4	14	12	17	1.5	1.1	2.8	4.6	5.1	7.6
	Mean	**5.3**	**5.1**	**5.0**	**33**	**43**	**49**	**26.9**	**34.3**	**32.9**	**26.7**	**30.5**	**34.7**	**4.3**	**4.3**	**4.4**	**12**	**9**	**10**	**1.6**	**0.9**	**1.5**	**5.2**	**5.5**	**5.9**
6.5	0	6.4	6.4	6.9	23	21	12	3.2	4.3	3.9	10.1	9.1	9.6	3.8	3.8	3.7	11	11	5	0.9	0.7	0.5	5.8	6.1	5.0
	50	6.5	6.4	6.7	48	32	6	10.0	8.8	7.7	14.2	19.9	14.2	4.8	5.0	4.6	11	10	14	1.1	1.0	0.9	6.4	5.7	5.2
	100	6.3	6.0	6.5	48	56	38	21.6	28.4	11.9	32.2	37.8	26.0	5.0	4.8	4.6	17	13	19	2.2	1.2	1.3	7.5	6.2	8.1
	200	6.1	6.3	6.4	22	77	63	47.1	31.0	29.8	47.0	51.1	39.8	4.9	4.5	4.9	23	14	28	1.7	1.7	1.5	6.5	6.7	8.2
	Mean	**6.3**	**6.3**	**6.6**	**35**	**47**	**30**	**20.5**	**18.1**	**13.3**	**25.9**	**29.5**	**22.4**	**4.6**	**4.5**	**4.4**	**15**	**12**	**17**	**1.5**	**1.1**	**1.1**	**6.6**	**6.2**	**6.6**
																					P values				
																		pH	**<0.001**		**<0.001**		**0.00**		**<0.001**
																		P rate	0.79		**<0.001**		**<0.001**		0.06
																		Species	0.98		0.46		**0.02**		0.55
																		pH × P rate	0.98		0.50		0.49		0.52
																		pH × Species	0.99		0.50		0.17		0.92
																		P rate × Species	1.00		0.39		0.53		0.21
																		pH × P rate × Species	0.85		0.51		0.28		0.44

6.3.3 Plant P assimilation

In order to evaluate the potential for lotus to assimilate more P from the soil than ryegrass and clover, plant TP was analysed (Table 6.3). From the ANOVA, it was evident that mean herbage TP differed between species, and was affected by rate, pH and the interaction of all of these terms. There was no difference between species herbage TP at pH 4.5, however ryegrass TP at pH 5.5 was significantly higher, indicating the species has an appreciably better P uptake capacity than lotus or clover which were of similar values. Hinsinger and Gilkes (1996) have shown that P uptake from other species of ryegrass can be significantly greater than clover. An increase in herbage TP with soil P has been reported in other studies (Christie and Moorby 1975) and in line with Trolove et al. (1996), TP concentrations were similar in herbage from unfertilised lysimeters. Increasing soil pH had an effect of increasing herbage TP in clover and lotus. Ryegrass TP was greatest at pH 5.5, but pH 6.5 was significantly higher than 4.5. This could have simply been due to a greater uptake of P at higher pH levels where growth is optimal, and because inorganic P uptake of plants has been shown to be highest between pH 5 and 6 (Schachtman et al 1998). For the last harvest, plant dry matter yield was different between species (Figure 6.1), with ryegrass herbage equivalent or greater to other species at all pH levels and P rates, and lotus herbage yield was equivalent to clover (only lower at pH 4.5, 200 kg P ha^{-1}). Ryegrass yield was influenced by rate, particularly at low pH. This indicates that P had become limiting at low pH treatment, likely the consequence of elevated FRP losses from these soils compared to pH 5.5 and 6.5 treatments (Table 6.2).

Table 6.2. Mean proportion of FRP losses in final leachate as a percentage of starting leachate losses for clover, lotus and ryegrass treatments at pH 4.5, 5.5 and 6.5 and SSP rates of 0, 50 100 and 200 kg P ha^{-1}. Corresponding *P* values (significant if bold) are given for the comparison of means by plant species, pH and fertiliser rate, and for the interaction of these treatments.

Soil pH	Fertiliser rate (kg P ha^{-1})	Proportion of starting FRP (%)		
		Clover	Lotus	Ryegrass
4.5	0	13	13	7
	50	25	4	12
	100	3	5	7
	200	6	11	4
5.5	0	9	8	12
	50	6	4	6
	100	11	9	15
	200	5	12	5
6.5	0	13	27	20
	50	23	20	20
	100	22	9	28
	200	12	11	26
--------------------*P* values	--------------------			
pH	**< 0.001**			
Rate	0.387			
Species	0.480			
pH × rate	0.274			
pH × species	0.258			
Rate × species	0.095			
pH × rate × species	0.229			

Table 6.3. Mean herbage TP for clover, lotus and ryegrass treatments at pH 4.5, 5.5 and 6.5 and SSP rates of 0, 50 100 and 200 kg P ha^{-1}. Corresponding *P* values (significant if bold) are given for the comparison of means by plant species, pH and fertiliser rate, and for the interaction of these treatments.

Soil pH	Fertiliser rate (kg P ha^{-1})	Plant total P (mg P kg^{-1})		
		Clover	Lotus	Ryegrass
4.5	0	1479	1635	1293
	50	1325	1852	1583
	100	2048	2345	1735
	200	3755	2062	2567
5.5	0	2990	2781	3012
	50	2733	3468	5145
	100	4066	3417	6777
	200	3949	4625	8475
6.5	0	2623	3668	3034
	50	3644	3813	4378
	100	4345	4476	4821
	200	3744	4624	4765
----------------------*P* values ----------------------				
pH	<0.001			
Rate	<0.001			
Species	<0.001			
pH × rate	0.003			
pH × species	<0.001			
Rate × species	0.008			
pH × rate × species	<0.001			

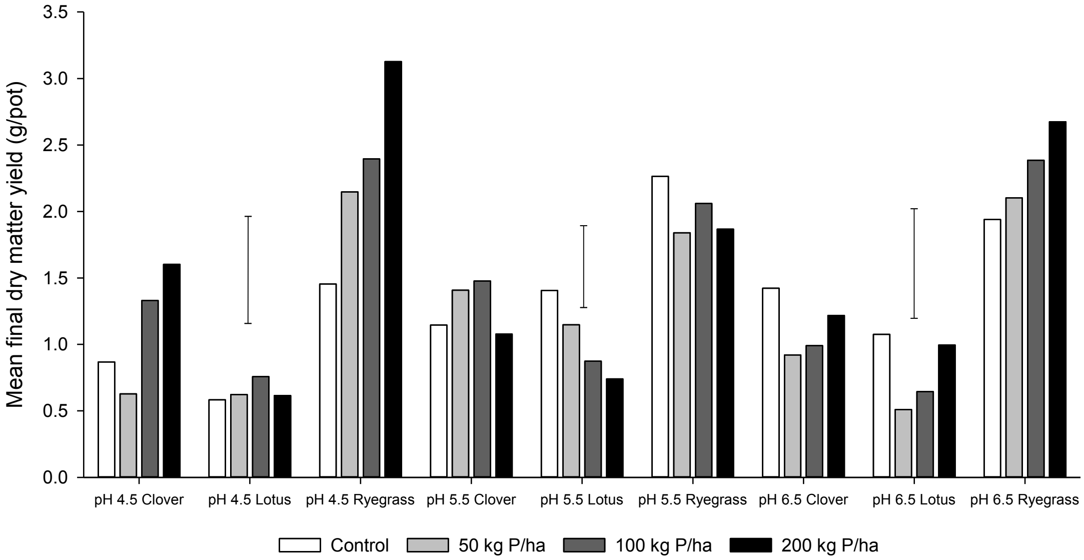

Figure 6.1. Mean final herbage yield for each species, fertiliser rate and soil pH. The least significant difference at the P<0.05 level is given for comparisons of species and P rate at each pH level.

6.4 Conclusions

Our hypothesis was that productivity and P losses are better in a lotus-based pasture than a clover or ryegrass-based pasture when at a pH and Olsen P representative of unmodified Organic soil. Comparisons of the relative decline in mean FRP losses in leachate over the 5 month trial showed that differences in FRP release were related to soil pH rather than plant species. Plant P was related to species, soil pH and P rate and their interactions. Data suggested that at pH levels approximating unmodified Organic soil (pH 4.5) there was no difference in plant P between species. However at pH 5.5, ryegrass uptake was greater than lotus or clover. My findings suggest that P losses under clover and lotus pastures will be similar or greater than losses under ryegrass, and depend primarily on soil pH and P rate. Due to the poor performance of lotus and clover in this study, it is not possible to make meaningful comparisons of their usefulness as a pastoral species in monoculture or their ability to curb P losses from Organic soils at a catchment or farm scale. Additional work is required to determine how this dynamic might change where lotus and clover monocultures are established at more comparable levels to ryegrass, and leaching data reflects the full period of plant growth.

Chapter 7

The use of iron, aluminium and calcium sulphates as amendments to decrease P losses from Organic soils

7.1 Introduction

Drainage and the application of lime and fertiliser amendments to Organic soils can increase production for pastoral agriculture (for example, dairying). However, their high OM content can increase the risk of P losses relative to more mineral soils (Gjettermann et al. 2007). Soil organic matter has been found to decrease P retention in soils due to competition between dissolved organic compounds and P for sorption sites on the soil surface (Sibanda and Young 1986; Guppy et al. 2005). These sorption sites are influenced by Fe, Al and Ca (Lindsay 1979). These elements have been used in varying combinations to reduce dissolved P concentrations. For example, alum and modified zeolite have been used as flocculants and lake-bed capping agents (Al-binding) (McDowell et al. 2008; Gibbs and Özkundakci 2011); laterite and bauxite is used in wastewater to reduce P enrichment (Al and Fe-binding; Vlahos et al. 1989; Summers et al. 1996); and lime or gypsum can increase Ca-phosphate formation and decrease water solubility of P in soil (Moore and Miller 1994; Chepkwony et al. 2001; Lee et al. 2011).

While it is widely accepted that Al, Fe and Ca dominate P retention in mineral soils, less work has focused on the relative importance of these in soils that are naturally deficient in them, but high in OM. Some studies have measured P desorption from a single soil using a range of amendments (e.g. Moore and Miller 1994), or over a range of soils (e.g. Borggaard et al. 2005), but these studies did not elaborate on the importance of Al, Fe and Ca amendments for retaining P in relation to OM. Due to competition between organic compounds and P, there is a higher risk of P loss from OM-rich soils; hence it would be useful to quantify the relative importance of Al, Fe and Ca as amendments to reduce P losses, while accounting for the interaction of soil OM. McDowell and Condron (2004) showed that for mineral soils, WEP provided a good approximation of the potential for P losses in surface runoff, and that WEP concentrations were related to the Olsen P and anion storage capacity of a soil. More recent work on Organic soils has shown that the quantity of WEP is related to Olsen P, the degree of phosphate saturation (DPS) and C ($P < 0.001$, Adj. $R^2 = 0.84$; Simmonds et al. 2015). I hypothesise that amendments of Fe, Al and Ca will decrease P losses (measured against WEP of the unmodified soil sample), but the importance of each amendment will depend on soil pH which controls the precipitation of metal-phosphates and that WEP decreases in C-rich soils will be less influenced by amendments than those soils with lower C content.

7.2 Materials and methods

7.2.1 Study site

Sampling was undertaken in the southern-end of the Waituna catchment in Southland, New Zealand (46° 34′S/168° 36′E) where poorly-drained acid Organic, Gley and Podzols (USDA Taxonomy, Hemists, Aquepts and Aquods; (USDA Taxonomy, Hemists, Aquepts and Aquods; Hewitt 2010) predominate (Wilson 2011). Farming in the Waituna catchment is largely pastoral (mainly dairying). The collected soils had been previously classified in a previous trial (Simmonds et al. 2015) as per New Zealand soil taxonomy as Acid Fibric Organic (Invercargill and Otanomomo) and Perch-Gley Podzol (Kapuka, Tisbury and Tiwai) soils (Hewitt 2010). Seventy-five topsoils were selected for the present study for a high C content (C > 16%; Table 7.1).

Table 7.1. Mean, minimum and maximum values and standard errors for selected physico-chemical properties for the study soils.

	Total carbon (%)	Bulk density (g cm^3)	ASC (%)	pH	Total P (mg kg^{-1})	WEP (mg L^{-1})	Olsen P (mg L^{-1})	Fe* (mg kg^{-1})	Al* (mg kg^{-1})	Total Ca (mg kg^{-1})	DPS (%)
Min	16	0.19	0	3.0	62	0.01	3	181	364	936	1
Max	53	0.81	98	6.7	2331	1.63	155	5244	12080	28764	47
Mean	37	0.48	25	4.3	647	0.25	36	1532	2644	10286	12
Std. error	1	0.02	3	0.1	59	0.03	3	150	292	922	1

* Ammonium oxalate extractable.

7.2.2 Incubation set up and collection

Prior to incubation, samples were air-dried at 35°C, ground and sieved < 2 mm. Soils were analysed for pH (in water; Hendershot et al. 1993), Olsen P (Olsen 1954), TP (via perchloric-nitric acid digestion; Olsen and Sommers 1982), WEP (McDowell and Condron 2004), $CaCl_2$-P (McDowell and Condron 2004), organic C (Metson et al. 1979), ASC (Saunders 1965), and BD (Parent and Caron 1993). Concentrations of Al_{OX} and Fe_{OX}, representing the amorphous fractions of these elements able to adsorb P were determined by acid ammonium oxalate extraction and ICP-OES (McKeague and Day 1966; Breeuwsma et al. 1995). Total Ca was determined by perchloric-nitric acid digestion and was analysed by ICP-OES.

Prior to incubation, either 0.5M Aluminium Sulfate Octadecahydrate ($Al_2(SO_4)_3.18H_2O$), 0.1M Iron(II) Sulfate Heptahydrate ($FeSO_4.7H_2O$) or 0.5M Calcium Sulfate Dihydrate ($CaSO_4.2H_2O$) was added to 3 g duplicate samples of each soil in sufficient quantity to double the amorphous Al, Fe or total Ca content of that sample (calculated from ICP-OES of unamended soils). All samples were topped up to 10 mL with RO water and allowed to dry at 35°C, then rewetted (5 mL RO) to further allow amendments to dissolve and interact with the soil. This process was repeated three times over three weeks. To half of the soils, 3 mL of 5 ppm orthophosphate solution was added to create eight treatments (Ca+/-P; Al+/-P; Fe+/-P; and control+/-P). This P concentration was in line with other P sorption studies (Hedley et al. 1982; Dunne et al. 2005). The addition of the orthophosphate was followed by another three week equilibration period containing three wetting and drying cycles and yielded eight treatments for each of the 75 soils: (n = 600). After an incubation period of 6 weeks, dry soils were removed and measured for WEP, pH and Olsen P.

7.2.3 Statistical analyses

Best subsets regression modelling with Mallows Cp was used to determine the variables that best explained WEP concentration. All statistical analyses and summary statistics (mean, standard error and range) were performed using the statistical package GenStat version 16

(Payne et al. 2011). Data were log-transformed if not normally distributed. The threshold for statistical significance was $P < 0.05$.

7.3 Results and Discussion

7.3.1 Soil physical and chemical properties

Soil physical and chemical properties were highly variable (Table 7.1). On average, unamended soils in the study had high carbon content, a low bulk density and pH. Total P was moderate and Olsen P near optimal levels for agronomic production for Organic soils (35-45 mg P L^{-1}; Roberts and Morton 2009). However, soils were acidic, and had a moderate WEP. Mean Fe_{OX} and Al_{OX} concentrations were 1,532 and 2,644 mg kg^{-1}. Mean total Ca was 10,286 mg kg^{-1}.

7.3.2 The influence of mineral amendments and P additions on pH, Olsen P and WEP

An ANOVA showed that 5 ppm P additions increased WEP and Olsen P, while all amendments decreased mean WEP, Olsen P, and pH (Fig. 7.1; Table 7.2). Both Al and Fe sulphate have been shown to acidify soils (Haynes 1986). Aluminium sulphate caused the greatest decrease in WEP compared to control (39% and 44% decrease, with and without 5 ppm P, respectively), followed by Fe and Ca amendments which had a similar influence on WEP (29% and 24%, and 19% and 16% decreases, with and without 5 ppm P, respectively). The dominance of Al in reducing WEP, compared to Ca and Fe, is likely because unamended soils had a greater Al than Fe concentration due to the dominance of low lying and periodically inundated conditions that promote Fe leaching from top soils (Pant et al. 2002). Furthermore, while Al and Fe can act to reduce WEP via sorption reactions, Ca-phosphates arise and induce lower WEP concentrations only when at or above neutral soil pH (Lindsay 1979). Calcium phosphate precipitation can also be inhibited by organic compounds, and modify the availability of P in soils (Alvarez et al. 2004).

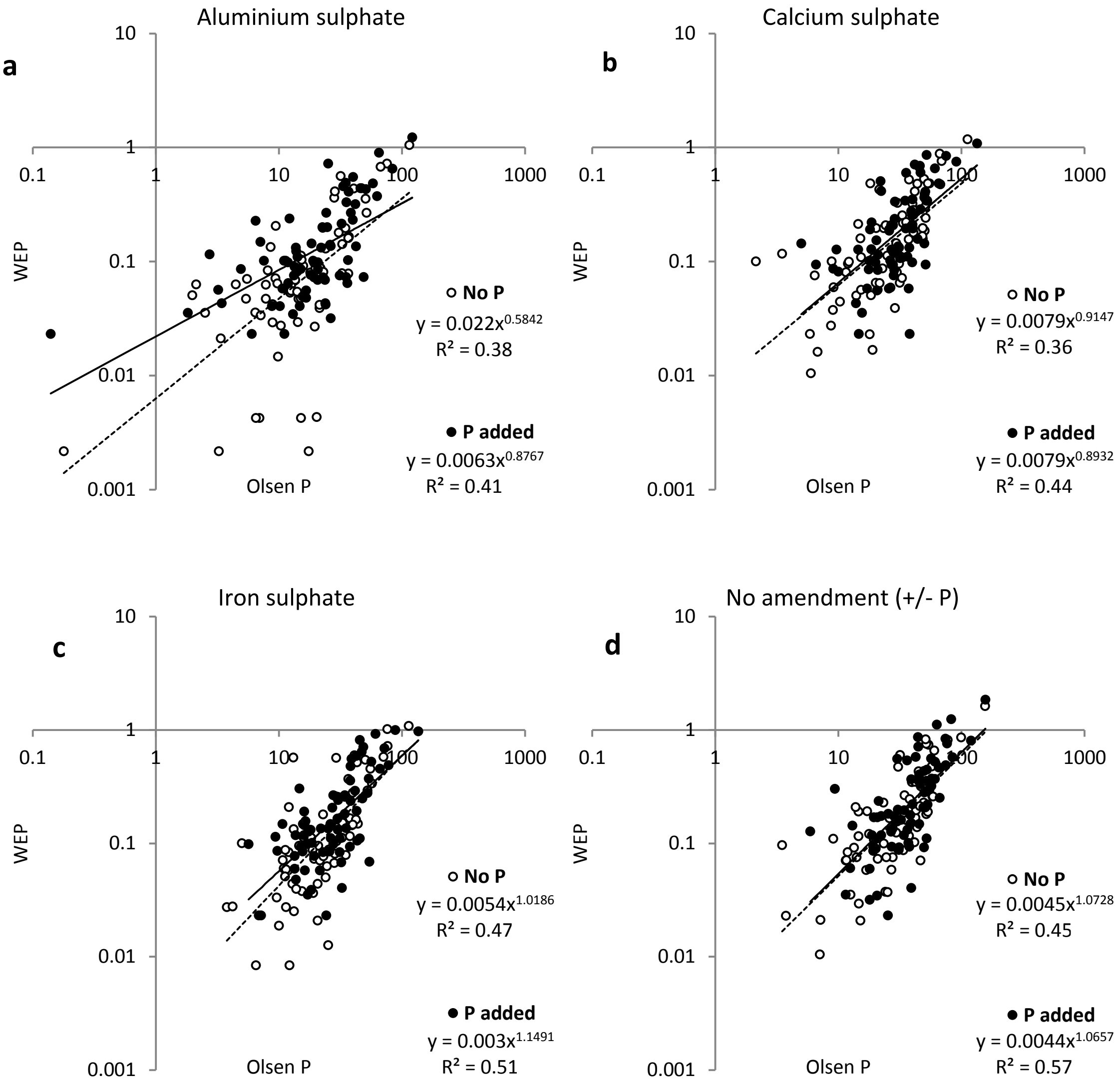

Figure 7.1. Plot of WEP concentration against Olsen P concentration for soils treated with amendments of (a) aluminium sulphate, (b) calcium sulphate, (c) iron sulphate and (d) no amendment. All with and without 5 ppm P added (solid/dotted trend line indicates presence/absence 5 ppm P solution). The slope and coefficient of determination for the regression fits to each data set are also given.

While the magnitude of soil Olsen P decrease in amended compared to the control soil was similar to WEP (1% difference between Olsen P and WEP change, on average), there was no difference between amendments (Table 7.2). This most likely reflects the inability of $NaHCO_3$ to extract potentially leachable P, instead being designed to extract plant available P from Al, Fe and Ca compounds (Chen et al. 2000; Condron and Newman 2011). Olsen P indicates plant available P fractions, so Al amendments could potentially limit P uptake by herbage by creating insoluble Al-P complexes. However for many plant species, organic acid root exudates can increase the mobility of Al-bound P for subsequent uptake (e.g. Shen et al. 2002). As with WEP, the relative dominance of Al in reducing Olsen P concentrations highlights the importance of Al for P retention in the soils of this catchment, compared to Fe and Ca.

Table 7.2. Mean, minimum and maximum values and standard errors (SE) for pH, Olsen P and WEP for soils receiving amendments of aluminium, iron (II) and calcium sulphate, and control soils, with and without additions of 5 ppm P solution. *F*-statistics are given for the comparison of treatment means by soil amendment, P fertiliser addition, and for interactions between soil amendment and P fertiliser addition.

		WEP (mg L^{-1})				Olsen P (mg L^{-1})				pH			
		Min	Max	Mean	SE	Min	Max	Mean	SE	Min	Max	Mean	SE
Without P	Al	0.00	1.05	0.14	0.023	0.2	114.7	21.0	2.3	2.5	6.1	3.5	0.1
	Fe	0.01	1.09	0.19	0.027	3.8	113.3	28.1	2.4	2.8	6.4	3.9	0.1
	Ca	0.01	1.18	0.21	0.026	2.1	112.0	29.2	2.4	2.8	6.5	4.0	0.1
	Control	0.01	1.63	0.25	0.033	3.5	155.4	36.1	2.9	3.0	6.7	4.3	0.1
With P	Al	0.02	1.23	0.19	0.025	0.1	121.6	25.0	2.3	2.3	6.2	3.5	0.1
	Fe	0.02	1.00	0.22	0.026	5.7	136.0	32.0	2.5	2.8	6.6	3.9	0.1
	Ca	0.02	1.08	0.25	0.027	5.0	134.6	34.5	2.4	2.8	6.5	3.9	0.1
	Control	0.02	1.85	0.31	0.037	5.9	156.9	41.7	2.9	3.1	6.9	4.3	0.1
	F statistics												
	Amendment				< 0.001				< 0.001				< 0.001
	P fertiliser				< 0.001				< 0.001				< 0.445
	Amend × P fertiliser				0.002				0.735				0.978

7.3.3 Factors contributing to WEP concentrations from amended soils

Pearson correlation coefficients were produced between WEP and physio-chemical properties (Table 7.3). Correlations were positive for DPS, total C and Olsen P, and were negative for ASC, BD and Al_{OX}. There was no difference in the number of correlated constituents among amendments or when P was added. These findings were in line with a previous study using a wider range of Organic and Podzol soils from the same catchment (Simmonds et al. 2015). Positive correlations with DPS (and by extension, Al_{OX} as it forms part of the DPS quotient) are to be expected, as DPS is commonly used as an indicator for the potential for soil to release P to surface runoff and leaching (e.g. Allen and Mallarino 2006; Amarawansha and Indraratne 2010). Similarly, a negative correlation between WEP and ASC is to be expected, as ASC describes the potential for P retention in soil (McDowell and Condron 2004). Water extractable P has been shown to have a close relationship with Olsen P (McDowell and Sharpley 2001). As with the Simmonds et al. (2015) study, Fe_{OX} was not correlated with WEP, most likely due to Fe leaching from these soils under the wet and reductive conditions that occur in Organic and Podzol soils (Pant et al. 2002). There was a trend of decreasing Al_{OX}, Fe_{OX} and total Ca (and therefore P sorption) with increasing C (Figure 7.2; $P < 0.05$), explaining the positive relationship between WEP and total C ($P < 0.01$; Figure 7.3 a-d). High C concentrations in soils have also been known to create competition between DOC compounds and orthophosphate ions, further limiting the ability of the soils to retain P (e.g. Mengel 2008). It was impossible to tell whether C or Al was the dominant factor or just the corollary of one-another. However, Borggaard et al. (2005) tested the influence of humic substances on the P sorption capacity of several Al and Fe compounds. Their trial compared P retention in washed and unwashed soils (a process designed to remove organic compounds responsible for interference with P sorption sites), and found changes in P sorption were a function of Al, more than Fe concentration, and were not strongly influenced by organic compounds.

Table 7.3. Pearson correlation coefficients between WEP and selected physiochemical properties for all amendments, with and without 5 ppm P solution (bold if significant to $P < 0.05$).

Physiochemical property	WEP Al	WEP Ca	WEP Fe	WEP control	WEP+P Al	WEP+P Ca	WEP+P Fe	WEP+P control
ASC (%)	**-0.412**	**-0.458**	**-0.436**	**-0.428**	**-0.393**	**-0.451**	**-0.459**	**-0.389**
Bulk density (g cm^{3})	**-0.503**	**-0.524**	**-0.548**	**-0.473**	**-0.505**	**-0.568**	**-0.544**	**-0.510**
CaCl$_2$-P (mg L^{-1})	-0.107	-0.133	-0.109	-0.129	-0.132	-0.164	-0.145	-0.184
DPS (%)	**0.767**	**0.744**	**0.750**	**0.731**	**0.723**	**0.678**	**0.674**	**0.678**
Total C (g kg^{-1})	**0.379**	**0.364**	**0.373**	**0.321**	**0.335**	**0.358**	**0.383**	**0.308**
Total P (mg kg^{-1})	0.132	0.148	0.131	0.196	0.201	0.216	0.183	**0.244**
Total Ca (mg kg^{-1})	-0.067	-0.059	-0.077	-0.021	-0.091	-0.122	-0.147	-0.015
Al* (mg kg^{-1})	**-0.364**	**-0.388**	**-0.372**	**-0.357**	**-0.316**	**-0.355**	**-0.363**	**-0.305**
Fe* (mg kg^{-1})	-0.143	-0.067	-0.102	-0.044	-0.112	-0.050	-0.166	-0.007
Mn* (mg kg^{-1})	0.080	0.174	0.067	0.190	0.126	0.185	0.072	0.177
P* (mg kg^{-1})	-0.073	-0.022	-0.059	0.016	-0.028	0.003	-0.071	0.042
pH	0.129	0.142	0.144	0.198	0.118	0.151	0.099	0.167
Olsen P control (mg L^{-1})	**0.768**	**0.818**	**0.752**	**0.838**	**0.757**	**0.767**	**0.722**	**0.822**
WEP control (mg L^{-1})	**0.908**	**0.962**	**0.921**		**0.910**	**0.908**	**0.902**	**0.940**

*Ammonium oxalate-extractable

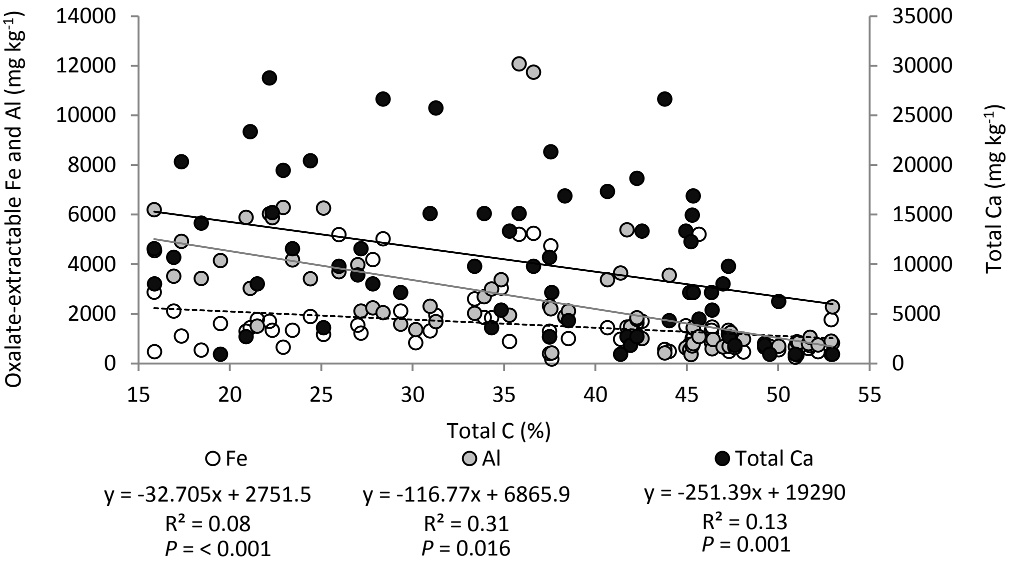

Figure 7.2. Plots of total soil carbon against oxalate-extractable Fe and Al, and total Ca. The slope and coefficient of determination for the regression and trend line fits to Fe (dotted), Al (grey) and total Ca (black) are also given.

A step-wise regression was carried out to determine the variables responsible for the most variation in WEP (Table 7.4). For all amendments, variability in WEP concentrations were associated with Olsen P, DPS, bulk density, and pH ($P < 0.001$; adj. $R^2 = 0.91$; Eq. 1). Soil bulk density decreases as organic matter increases (Perie and Ouimet 2008). The negative correlation between BD and WEP is therefore explained by the decreasing quantity of Al, Fe and Ca with increasing ratio of C ($P < 0.05$; Figure 7.2). The negative relationship between WEP and pH could be caused by the addition of amendments which decreased pH (Table 7.2), potentially altering the solubility of Al-, Fe- or Ca-phosphate. As described above, the positive relationships that were measured between DPS and WEP, and Olsen P and WEP are to be expected as correlations between these variables have been reported in earlier studies (e.g. Allen and Mallarino 2006; McDowell and Sharpley 2001).

$$WEP_{AVG} = 0.01 \times DPS + 0.005 \times \text{Olsen P} - 0.42 \times BD - 0.05 \times pH + 0.36 \qquad \text{[Eq. 1]}$$

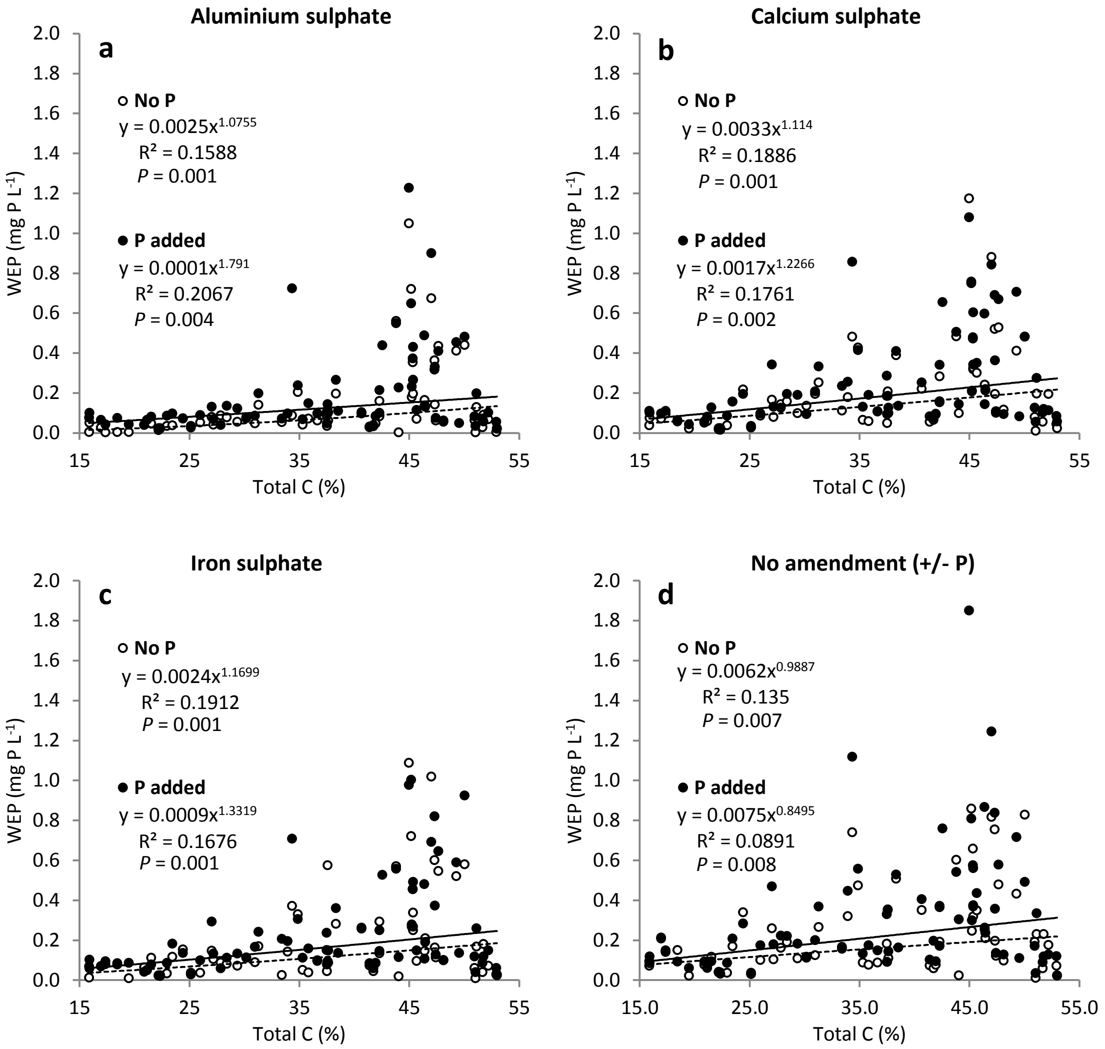

Figure 7.3. Plot of WEP concentration against total C for soils treated with amendments of (a) aluminium sulphate, (b) calcium sulphate, (c) iron sulphate and (d) no amendment. All with and without 5 ppm P added (solid/dotted trend line indicates presence/absence 5 ppm P solution). The slope and coefficient of determination for the regression fits to each data set are also given.

Table 7.4. Coefficient values for WEP predictive terms from stepwise regression analyses. WEP$_{AVG}$ is an average of the WEP values across all treatment for each soil.

	R^2 (adj)	Bulk dens. (g cm^{3})	DPS (%)	pH	Olsen P (mg P L^{-1})	Constant
WEP$_{Con}$	0.87	-0.44	0.009	n/a	0.008	0.30
WEP$_{Al}$	0.90	-0.36	0.013	-0.05	0.005	0.25
WEP$_{Fe}$	0.84	-0.46	0.01	-0.22	0.005	0.91
WEP$_{Ca}$	0.91	-0.41	0.01	-0.06	0.006	0.37
WEP$_{AVG}$	0.91	-0.42	0.01	-0.05	0.005	0.36

7.4 Conclusions

The magnitude of WEP decrease was dependent on the initial Al, Fe and Ca concentration of the soil. However, on average, the response in WEP to doubling the concentration of Al and Fe was more effective than adding Ca (i.e. without changing pH as would happen if added as lime). My secondary hypothesis was that WEP losses from C-rich soils will be less influenced by amendments than those soils with lower C content. Although the Pearson test showed total C was positively correlated with WEP (Table 7.3), and that WEP was highly variable at greater C levels (Figure 7.3 a-d), components other than C (but perhaps acting as a surrogate) better described variation in WEP. Thus, it cannot be concluded that OM had a greater influence on WEP concentrations than other components. These findings suggest that even in C-rich soils, what little Al and Fe is present in the soil is highly influential in determining WEP concentrations. The concentration of Al and Fe could be altered with amendments to decrease WEP and the potential for loss to surface and groundwaters.

Chapter 8

Summary and future research priorities

8.1 Summary of results and implications for P loss mitigation

The conversion of Organic soils for intensive agriculture carries a high risk for P export from the landscape, yet marginal soil development is increasing globally due to population growth and a demand for agricultural products. The overall hypothesis for this body of work was that P losses from Organic soils and potential water quality impacts are high, especially after initial development, but will decrease due to changes in soil properties and better management. The main aims of this thesis were to identify which properties of Organic soils best indicate the potential scale of P losses, the timeframe over which the risk of P losses is greatest, and how soil and land management variables including soil moisture, liming and fertiliser rates, fertiliser solubility, and mineral content can influence the quantities, forms and fractions of P exported from the landscape.

The first step was to collect physicochemical and management data for ninety soils from the lower Waituna catchment – a predominantly dairying-oriented catchment populated by poorly-drained Organic, Podzol and Gley soils. This data was used to determine how the potential for topsoil and subsoil P losses from an array of soils changed over time (since development from scrub), and what physical, chemical and management properties those losses were related to. It was found that for Organic soils, P losses were immediately high following development, and P concentrations in overland flow (as WEP) could be approximated by Olsen P, DPS (as oxalate-extractable concentrations of Fe, Al and P), and the C content of the soil. This was important because it helped fill a potential knowledge gap in previous work by McDowell and Condron (2004), who found that WEP in overland flow from mineral soils was a function of Olsen P and ASC. The findings of that trial enabled us to create terms for the prediction of surface losses from Organic and Podzol soils, and subsurface losses (as $CaCl_2$-P) from Podzol soils. The data also demonstrated that Organic soils have the potential to lose more P than a Podzol soil.

The findings of this study indicated that Organic soils are prone to high P losses immediately following development, and that efforts to mitigate P losses should be employed at this time. I then set about determining what soil attributes and environmental conditions are most influential to P losses, and how soil management practices commonly practiced over that timeframe (including liming, fertiliser application and pastoral species) could be optimised to reduce P losses, with minimal detrimental impact to productivity.

A runoff trial was conducted to assess the most important pathway for P loss from an acid Organic soil and acid Mesic Brown soil at different soil moisture levels and Olsen P fertility. The data suggested that for Brown soils, high soil moisture (>90% AWHC) can lead to an elevated potential for P losses in overland flow via saturation-excess surface runoff. Because of a high ASC, P was primarily lost as PP from these soils, rather than in dissolved forms. Surface runoff was also generated from dry Organic soils, but this was due to hydrophobicity (infiltrations-excess surface runoff). Similarly to Brown soils, PP was transported in surface runoff, but due to a very low ASC, a much greater proportion of the P lost was in dissolved form, and was an order of magnitude greater than equivalent Brown soils. However, due to a high hydraulic conductivity and low ASC the greatest quantity of P lost from Organic soil (regardless of moisture) was via subsurface flow; found to be between 77 and 100 times greater than mean P losses in surface flow, primarily as dissolved forms. This work indicates that strategies to reduce P losses from Organic soils should account for leachate or drainage being the dominant pathway of P loss, and should be field tested to confirm.

Management decisions for recently developed Organic soil typically include liming to correct acidic soil conditions, capital applications of P fertiliser to increase plant-available P, and the establishment of hardy pastoral species. To this end, three lysimeter trials were conducted to determine how these management decisions might be optimised to reduce P losses in leachate. All lysimeter trials were conducted at three pH levels (4.5, 5.5 and 6.5) and four P rates (0, 50, 100 and 200 kg P ha^{-1}) over 12 months in temperature and precipitation-controlled greenhouse.

A lysimeter trial was carried out to assess the quantity of P fractions in leachate, and soil as a function of soil pH (controlled by liming). I had hypothesised the quantity of P in leachate would increase with soil pH and fertiliser P rate. The data showed that most P was lost from pH 4.5 soils. Soil P fractionation data revealed that due to very low quantities of Fe and Al-oxides, P was retained in limed soils by the creation of Ca-phosphates that were readily soluble in HCl. This contrasted with other studies that had found that raising soil pH increased the solubility of Fe and Al-phosphates. As the higher pH increased ryegrass production, this also resulted in a higher quantity of P in plant biomass at pH 5.5 and 6.5. The results show that P losses from mineral-deficient Organic soils can be mitigated in the short term by the addition of lime to increase soil pH to > 5.5.

The second lysimeter trial compared P losses in leachate following the application of a soluble P fertiliser and a sparingly soluble fertiliser (RPR). The results of this trial showed that at low pH, P losses in leachate were greatest for both fertiliser types and the cost of P losses from SSP were 94% higher than RPR. As pH increased, the cost of P losses from SSP also increased, compared to RPR (252% higher at pH 6.5). There were no significant differences in plant growth at pH 4.5 and 5.5; however at pH 6.5 mean SSP yield was 7% greater than RPR. This trial showed that P losses in leachate can be significantly lower from an acid, Organic soil that is limed to pH > 5.5, when RPR is used over SSP.

The third lysimeter trial attempted to compare plant productivity and P losses in leachate from three pastoral species – greater lotus, white clover and perennial ryegrass. Lotus had previously been shown to be tolerant to low pH and limited nutrients, which could yield a productive advantage over more commonly opted legume and grass pasture species (e.g. white clover and ryegrass) on a recently developed acid Organic soil. However, issues with the watering system and fungus gnat infestations severely limited the growth of lotus and clover. Due to the poor performance of these species it was difficult to make any meaningful comparisons of their relative usefulness as a pastoral species in monoculture or their ability to curb P losses from Organic soils. Further work is therefore required to compare these species effectively.

The primary study found that while P release as WEP in surface runoff was a function of Olsen P, DPS and C, there was no effective prediction term for subsurface P losses (estimated by $CaCl_2$-P; McDowell and Condron 2004). However, from subsequent lysimeter trials it was clear that ASC (or DPS, as a function of Al, Fe and Ca concentrations) was key in controlling the magnitude of P losses from Organic soil in both overland and subsurface flow. To this end, an incubation trial that doubled the concentrations of metal oxides (Fe, Al and Ca) in 75 topsoils over a range of C and Olsen P values (with and without added P) was conducted. The objective was to double the natural amorphous concentrations of Al, Fe or Ca, with and without additional P, in order to determine the roles of these minerals in regulating surface P losses (measured as WEP) in relation to soil carbon (C). The results showed no strong relationship between C and WEP, and found Al was the most important metal oxide controlling WEP concentrations for soils of the catchment, and indicated that amendments of an Al-based material could significantly reduce P transport from the soil.

In conclusion the potential for P losses from Organic soils was confirmed to be high immediately following development and via subsurface flow. However, the scale of these losses can be predicted with simple soil tests, and where necessary, can be better managed by increasing P sorption in the soil (e.g. liming to pH > 5.5 or other soil amendments, e.g. alum) and through the use of sparingly soluble P fertilisers.

8.2 Future research priorities

This body of work has demonstrated that P losses from Organic soils are high following development, and occur through subsurface pathways. It has detailed best management practices that mitigate P losses at a management scale including higher liming rates, low-solubility P fertiliser and pasture species that provide a balance of high P uptake and yield with little P inputs. The following section proposes additional work that could address gaps in this research.

8.2.1 Establish the use of $CaCl_2$ as a measure for estimating subsurface P losses from Organic soils

Chapter 2 used soil properties and management variables to develop a predictive equation for WEP losses from Organic soils (an indication of surface P loss potential in overland runoff), but was not able to establish a workable equation for $CaCl_2$-P losses (P loss potential in subsurface runoff) using the same set of variables. This research and others (McDowell et al. 2002) have shown that $CaCl_2$ extracts P from different pools and at different quantities compared to water, however the use of $CaCl_2$-P as a measure of sub-surface losses has not been verified for Organic soils as with more mineral soils (McDowell and Condron 2004). In order to predict $CaCl_2$-P from soil and land management variables (as with WEP), it must first be determined if $CaCl_2$-P is a useful measure of estimating sub-surface losses from Organic soils.

8.2.2 Strategic application of lime, Al or plant species to reduce P losses from critical source areas

Chapter 3 found that the majority of P transport from soils occurred in subsurface flow, and later chapters provided some management oriented strategies to reduce those losses. However hydrophobic Organic soils still lost approximately 30% of their total P in overland flow as a combination of PP and FRP. Following this, chapter 4 established that in the absence of P-sorbing metal oxides found in mineral soils, the application of higher rates of lime had the effect of decreasing the quantities of P released from Organic soil due to the formation of Ca-phosphates that were poorly-soluble at higher pH levels. Chapter 7 found that doubling the Al_{ox} content of OM-rich soils required only small additions of alum (due to naturally low soil concentrations) yet resulted in a mean WEP decrease of 87% compared to controls. The cost of liming to pH > 5.5 or broadly applying alum may be prohibitive on a whole farm, yet an alternative strategy could be liming or applying alum at higher rates in critical source areas (CSAs) to intercept overland or drainage P losses. Following this, part of the logic of chapter 6 was that lotus supposedly had a higher P uptake capacity than clover or ryegrass, and that this could lead to lower P losses. This was not demonstrated, however the principle remains, that a high P uptake plant could potentially be used in CSAs to intercept nutrients and provide feed for stock. The potential ecological and economic implications of these mitigation strategies need to be explored.

8.2.3 Test the environmental and economic limitations of alum amendments on Organic soils

Chapter 7 demonstrated excellent potential for Al amendments to reduce WEP from an array of Organic soils. However, Al-toxicity is a major limitation to crop growth, and is a primary reason why liming is undertaken (Haynes and Mokolobate; 2001), and McDowell (2010) assessed the use of alum (20 kg ha^{-1}) to reduce P losses from a high-rainfall environment, but P retention was not significantly increased due to the removal of alum by precipitation. Further work is needed to determine if the small quantities of Al used in chapter 7 would increase P retention *in situ*, potentially using different Al forms or application methods. Then test any effects to feed quality, herbage yield, or environmental risk when applied as a soil amendment.

8.2.4 Determine quantity and bioavailability of PP losses in Organic soil drainage

Previous studies (e.g. Stamm et al. 1998) state that in some soils, subsurface flow pathways are important for transporting both dissolved and PP. This PP can eventually stimulate primary production and contribute to eutrophication symptoms. Due to the loosely-structured nature, high porosity and hydraulic conductivity of Organic soils, P losses via macropores are predictable, yet are hard to quantify. It would be valuable to determine the quantity and bioavailability of PP lost from Organic soils in subsurface pathways, and following this, to develop a strategy for reducing these losses. In this regard, applications of gypsum have shown promise (e.g. Svanbäck et al. 2014), and alternative materials that promotes aggregate formation and strength could also be explored.

References

Aalders I, Hough RL, Towers W 2011. Risk of erosion in peat soils – an investigation using Bayesian belief networks. Soil Use and Management 27: 538-549.

Abell J, Özkundakci D, Hamilton D 2010. Nitrogen and phosphorus limitation of phytoplankton growth in New Zealand lakes: implications for eutrophication control. Ecosystems 13: 966-977.

AgResearch 2013. Overseer® Nutrient Budgets v6.0: References and technical notes. Available at: http://www.overseer.org.nz/OVERSEERModel/Information/References.aspx (accessed April 2013).

Allen BL, Mallarino AP 2006. Relationships between extractable soil phosphorus and phosphorus saturation after long-term fertilizer or manure application. Soil Science Society of America Journal 70: 454-463.

Alvarez R, Evans LA, Milham PJ, Wilson MA 2004. Effects of humic material on the precipitation of calcium phosphate. Geoderma 118: 245-260.

Amarawansha EAGS, Indraratne SP 2010. Degree of phosphorous saturation in intensively cultivated soils in Sri Lanka. Tropical Agricultural Research 22: 113-119.

Anderson D, Glibert P, Burkholder J 2002. Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. Estuaries and Coasts 25: 704-726.

Andersson S, Nilsson SI 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. Soil Biology and Biochemistry 33: 1181-1191.

Anon 2010. European Communities (Good Agricultural Practice for Protection of Waters) Regulations 2010. SI 610 of 2010. Department of Environment, Heritage and Local Government. The Stationary Office, Dublin, Ireland: 54 p.

Anon 2013. Dairy soils and fertiliser manual. Chapter 9: Interpreting soil and tissue tests, Rosevear R, Kowitz R ed. Australian nutrient management guidelines. Department of Primary Industries, Victoria, Australia: 35 p.

ANZECC 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council-Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT.

Armentano TV 1980. Drainage of Organic soils as a factor in the world carbon cycle. BioScience 30: 825-830.

Arvidsson J 1998. Influence of soil texture and organic matter content on bulk density, air content, compression index and crop yield in field and laboratory compression experiments. Soil and Tillage Research 49: 159-170.

Asner GP, Elmore AJ, Olander LP, Martin RE, Harris AT 2004. Grazing systems, ecosystem responses, and global change. Annual Review of Environmental Resources 29: 261-299.

Ausseil AG, Jamali H, Clarkson BR, Golubiewski NE 2015. Soil carbon stocks in wetlands of New Zealand and impact of land conversion since European settlement. Wetlands Ecology and Management 23: 947-961.

Ball DF 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. Journal of Soil Science 15: 84-92.

Ballantine D, Booker D, Unwin M, Snelder T 2010. Analysis of national river water quality data for the period 1998-2007. NIWA Client Report CHC2010-038: 34 p.

Bennett EM, Carpenter SR, Caraco NF 2001. Human impact on erodable phosphorus and eutrophication: a global perspective. BioScience 51: 227-234.

Bennion H, Juggins S, Anderson N J 1996. Predicting epilimnetic phosphorus concentrations using an improved diatom-based transfer function and its application to lake eutrophication management. Environmental Science and Technology 30: 2004-2007.

Biemelt D, Schapp A, Kleeberg A, Grünewald U 2005. Overland flow, erosion, and related phosphorus and iron fluxes at plot scale: a case study from a non-vegetated lignite mining dump in Lusatia. Geoderma 129: 4-18.

Biggs BJF 2000. New Zealand periphyton guidelines: detecting, monitoring and managing enrichment of streams. New Zealand Ministry for the Environment publication: 122 p. Available from: http://www.mfe.govt.nz/publications/water/nz-periphyton-guide-jun00.pdf.

Bisdom EBA, Dekker LW, Schoute JFT 1993. Water repellency of sieve fractions from sandy soils and relationships with organic material and soil structure. Geoderma 56: 105-118.

Boelter DH 1968. Important physical properties of peat materials. Proceedings of the 3rd International Peat Congress, Quebec: 150-156.

Boelter DH 1969. Physical properties of peats as related to degree of decomposition. Soil Science Society of America Journal 33: 606-609.

Bolan NS, White RE, Hedley MJ 1990 A review of the use of phosphate rocks as fertilizers for direct application in Australia and New Zealand. Australian Journal of Experimental Agriculture 30: 297–313.

Borggaard OK, Jdrgensen SS, Moberg JP, Raben-Lange B 1990. Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. Journal of Soil Science 41: 443-449.

Borggaard OK, Raben-Lange B, Gimsing AL, Strobel BW 2005. Influence of humic substances on phosphate adsorption by aluminium and iron oxides. Geoderma 127: 270-279.

Borowiak D, Nowiński K, Barańczuk J, Skowron R, Solarczyk A, Marszelewski W 2010. Interactions between areal hypolimnetic oxygen depletion rate and trophic state of lakes in northern Poland. Limnological Review 11: 135-142.

Boruvka L, Rechcigl JE 2003. Phosphorus retention by the Ap horizon of a Spodosol as influenced by calcium amendments. Soil Science 168: 699-706.

Breeuwsma A, Reijerink JGA, Schoumans OF 1995. Impact of manure on accumulation and leaching of phosphate in areas of intensive livestock farming. In: Steele, K. (Ed.), Animal Waste and the Land–Water Interface. CRC Press, Boca Raton, USA: 239-249.

Brookes PC, Heckrath G, De Smet J, Hofman G, Vanderdeelen J 1997. Losses of phosphorus in drainage water. In Phosphorus loss from soil to water. Eds. Tunney H, Carton OT, Brookes PC, Johnston AE. Biddles Ltd, UK: 253-271.

Bryant RB, Buda AR, Kleinman PJA, Church CD, Saporito LS, Folmar GJ, Bose S, Allen AL 2012. Using flue gas desulfurization gypsum to remove dissolved phosphorus from agricultural drainage waters. Journal of Environmental Quality 41: 664-671.

Burkholder JM, Glasgow HB, Jr. 1997. *Pfiesteria piscicida* and other Pfiesteria-Like dinoflagellates: behavior, impacts, and environmental controls. Limnology and Oceanography 42: 1052-1075.

Burkitt LL, Donaghy DJ, Smethurst PJ 2010a. Low rates of phosphorus fertiliser applied strategically throughout the growing season under rain-fed conditions did not affect dry matter production of perennial ryegrass (*Lolium perenne* L.). Crop and Pasture Science 61: 353-362.

Burkitt LL, Dougherty WJ, Corkrey R, Broad S 2010b. Comparing the risk of phosphorus runoff following single and split phosphorus fertiliser application in two contrasting catchments using rainfall simulation and Bayesian modeling. In 19th World Congress of Soil Science, Soil Solutions for a Changing World, Brisbane, Australia: 20-23 p.

Butterly CR, Bünemann EK, McNeill AM, Baldock JA, Marschner P 2009. Carbon pulses but not phosphorus pulses are related to decreases in microbial biomass during repeated drying and rewetting of soils. Soil Biology and Biochemistry 41: 1406-1416.

Cameron K, Smith N, McLay C, Fraser P, McPherson R, Harrison D, Harbottle P 1992. Lysimeters without edge flow: An improved design and sampling procedure. Soil Science Society of America Journal 56: 1625-1628.

Carpenter SR, Bolgrien D, Lathrop RC, Stow CA, Reed T and Wilson MA 1998b Ecological and economic analysis of lake eutrophication by nonpoint pollution. Australian Journal of Ecology 23: 68-79.

Cassman KG, Dobermann A, Walters DT 2002. Agroecosystems, nitrogen-use efficiency, and nitrogen management. American Journal of Biology 31: 132-140.

Chang SC, Jackson ML 1957. Fractionation of soil phosphorus. Soil science 84: 133-144.

Charlton JFL, Brock JL 1980. Establishment of *Lotus pedunculatus* and *Trifolium repens* in newly developed hill country. New Zealand Journal of Experimental Agriculture 8: 243-248.

Chen CR, Condron LM, Davis MR, Sherlock RR 2000. Effects of afforestation on phosphorus dynamics and biological properties in a New Zealand grassland soil. Plant and Soil 220: 151-163.

Chen CR, Condron LM, Davis MR, Sherlock RR 2002. Phosphorus dynamics in the rhizosphere of perennial ryegrass (*Lolium perenne* L.) and radiata pine (Pinus radiata D. Don.). Soil Biology and Biochemistry 34: 487-499.

Chenu C, Le Bissonnais Y, Arrouays D 2000. Organic matter influence on clay wettability and soil aggregate stability. Soil Science Society of America Journal 64: 1479-1486.

Chepkwony CK, Harrison R, Swift RS 2001. Mineralization of soil organic P induced by drying and rewetting as a source of plant-available P in limed and unlimed samples of an acid soil. Plant and Soil 234: 83-90.

Childs CW, Searle PL, Wells N 1977. Infiltration through soil as a tertiary treatment of sewage effluent: chemical and biological measurements on leachates from undisturbed cores of ten New Zealand soils. New Zealand Soil Bureau Scientific Report 29: 87 p.

Chow GC 1960. Tests of equality between sets of coefficients in two linear regressions. Econometrica: Journal of the Econometric Society: 591-605.

Christie E, Moorby J 1975. Physiological responses of semiarid grasses. I. The influence of phosphorus supply on growth and phosphorus absorption. Crop and Pasture Science 26: 423-436.

Cleveland CC, Liptzin D 2007. C: N: P stoichiometry in soil: is there a “Redfield ratio” for the microbial biomass? Biogeochemistry 85: 235-252.

Codd GA 2000. Cyanobacterial toxins, the perception of water quality, and the prioritisation of eutrophication control. Ecological Engineering 16: 51-60.

Condron, L, Newman S 2011. Revisiting the fundamentals of phosphorus fractionation of sediments and soils. Journal of Soils and Sediments 11: 830-840.

Cooke JG, Stub L, Mora N 1992. Fractionation of phosphorus in the sediment of a wetland after a decade of receiving sewage effluent. Journal of Environmental Quality 21: 726-732.

Cornforth IS 1998. The fate of phosphate fertiliser in soils. In Chemical processes in New Zealand. Eds. Packer JE, Robertson J, Wansbrough H. New Zealand Institute of Chemistry: 12 p.

Curran Cournane F, McDowell RW, Condron LM 2010. Effects of cattle treading and soil moisture on phosphorus and sediment losses in surface runoff from pasture. New Zealand Journal of Agricultural Research 53: 365-376.

Curtin D, Syers JK 2001. Lime-induced changes in indices of soil phosphate availability. Soil Science Society of America Journal 65: 147-152.

Darke AK, Walbridge MR 2000. Al and Fe biogeochemistry in a floodplain forest: Implications for P retention. Biogeochemistry 51: 1-52.

de Mars H, Wassen MJ 1999. Redox potentials in relation to water levels in different mire types in the Netherlands and Poland. Plant Ecology 140: 41-51

DeBano LF 1981. Water repellent soils: a state-of-the-art. US Department of Agriculture, Forest Service, Pacific Southwest Forest and Range Experiment Station: 21 p.

Dekker LW, Ritsema CJ 1996. Variation in water content and wetting patterns in Dutch water repellent peaty clay and clayey peat soils. Catena 28: 89-105.

Dekker LW, Ritsema CJ 2000. Wetting patterns and moisture variability in water repellent Dutch soils. Journal of Hydrology 231–232: 148-164.

Deurer M, Müller K 2010. Towards a better understanding of the causes, effects and remediation of soil hydrophobicity. A report by Plant and Food Research to Regional Councils. 94 p.

Deurer M, Müller K, Van Den Dijssel C, Mason K, Carter J, Clothier BE 2011. Is soil water repellency a function of soil order and proneness to drought? A survey of soils under pasture in the North Island of New Zealand. European Journal of Soil Science 62: 765-779.

Dodds WK 2003. The role of periphyton in phosphorus retention in shallow freshwater aquatic systems. Journal of Phycology 39: 840-849.

Doerr SH, Shakesby RS, Walsh RPD 2000. Soil water repellency: its characteristics, causes and hydro-geomorphological consequences. Earth Science Reviews 51:33–65.

Dougherty WJ, Burkitt LL, Corkrey R, Harvey DM 2011. The effect of soil P sorption properties and phosphorus fertiliser application strategy on 'incidental' phosphorus fertiliser characteristics: a laboratory study. Nutrient Cycling in Agroecosystems 89: 189-197.

Drewry JJ, Littlejohn RP, Paton RJ 2000. A survey of soil physical properties on sheep and dairy farms in southern New Zealand. New Zealand Journal of Agricultural Research 43: 251-258.

Dumanski J, Pieri C 2000. Land quality indicators: research plan. Agriculture, Ecosystems and Environment 81: 93-102.

Dunne EJ, Culleton N, O'Donovan G, Harrington R, Daly K 2005. Phosphorus retention and sorption by constructed wetland soils in Southeast Ireland. Water Research 39: 4355-4362.

Dunne T, Black RD 1970. Partial Area Contributions to Storm Runoff in a Small New England Watershed. Water Resources Research 6: 1296-1311.

Edmeades DC, Metherell AK, Waller JE, Roberts AHC, Morton JD 2006. Defining the relationships between pasture production and soil P and the development of a dynamic P model for New Zealand pastures: A review of recent developments. New Zealand Journal of Agricultural Research 49: 207-222.

Ehrlich PR, Holdren JP 1971. Impact of population growth. Science 171: 1212-1217.

Eisenreich SJ, Bannerman RT, Armstrong DE 1975. A simplified phosphorus analysis technique. Environmental Letters 9: 43-53.

Environment Southland 2012. Catchment flow data logger information, Waituna Creek Marshall Road.

Eriksson AK, Ulén B, Berzina L, Lital A, Janssons V, Sileika AS, Toomsoo A 2013. Phosphorus in agricultural soils around the Baltic Sea – comparison of laboratory methods as indices for phosphorus leaching to waters. Soil Use and Management 29: 5-14.

Ferguson JF, Jenkins D, Eastman J 1973. Calcium phosphate precipitation at slightly alkaline ph values. Water Environment Federation 45: 620-631.

Foley JA, DeFries R, Asner GP, Barford C, Bonan G, Carpenter SR, Chapin FS, Coe MT, Daily GC, Gibbs HK, Helkowski JH, Holloway T, Howard EA, Kucharik CJ, Monfreda C, Patz JA, Prentice IC, Ramankutty N, Snyder PK 2005. Global consequences of land use. Science 309: 570-574.

Föllmi KB, Hosein R, Arn K, Steinmann P 2009. Weathering and the mobility of phosphorus in the catchments and forefields of the Rhône and Oberaar glaciers, central Switzerland: Implications for the global phosphorus cycle on glacial–interglacial timescales. Geochimica et Cosmochimica Acta 73: 2252-2282.

Forgy EW 1965. Cluster analysis of multivariate data: efficiency versus interpretability of classifications. Biometrics 21: 768–769.

Frossard E, Brossard M, Hedley MJ, Metherell A 1995. Reactions controlling the cycling of P in soils. In Phosphorus in the global environment. transfers, cycles and management. Ed. Tiessen H. pp 107-137. Wiley Publishers, Chichester.

Gibbs HS 1980. New Zealand soils, an introduction. Wellington, Oxford University Press: 115 p.

Gibbs M, Özkundakci D 2011. Effects of a modified zeolite on P and N processes and fluxes across the lake sediment–water interface using core incubations. Hydrobiologia 661: 21-35.

Gilbert N 2009. The disappearing nutrient. Nature 461: 716-718.

Gjettermann B, Styczen M, Hansen S, Borggaard OK, Hansen HCB 2007. Sorption and fractionation of dissolved organic matter and associated phosphorus in agricultural soil. Journal of Environmental Quality 36: 753-763.

Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environmental Science and Technology 28: 38-46.

Guérin J, Parent L-É, Si B 2011. Spatial and seasonal variability of phosphorus risk indexes in cultivated Organic soils. Canadian Journal of Soil Science 91: 291-302.

Gunn J, Sein R, Keller B, Beckett P 2001. Liming of acid and metal contaminated catchments for the improvement of drainage water quality. Water, Air, and Soil Pollution 130: 1439-1444.

Guppy CN, Menzies NW, Moody PW, Blamey FPC 2005. Competitive sorption reactions between phosphorus and organic matter in soil: a review. Soil Research 43: 189-202.

Gustafsson JP, Mwamila LB, Kergoat K 2012. The pH dependence of phosphate sorption and desorption in Swedish agricultural soils. Geoderma 189-190: 304-311.

Hannaway D, Fransen S, Cropper J, Teel M, Chaney M, Griggs T, Halse R, Hart J, Cheeke P, Hansen D, Klinger R, Lane W 1999. Perennial ryegrass (*Lolium perenne* L.). Oregon State University Extension Publication PNW503.

Harrison AF 1987. Soil organic phosphorus: a review of world literature. C.A.B. International, Wallingford: 257 p.

Haygarth PM, Chapman PJ, Jarvis SC, Smith RV 1998. Phosphorus budgets for two contrasting grassland farming systems in the UK. Soil Use and Management 14: 160-167.

Haygarth PM, Bardgett RD, Condron LM 2013. Phosphorus and nitrogen cycles and their management. In: Russell's Soil Conditions and Plant Growth - 12th Edition. Eds. Gregory PJ, Nortcliff S. Wiley-Blackwell, London, UK: 132–159.

Haygarth PM, Condron LM 2004. Background and elevated phosphorus release from terrestrial environments. In: Phosphorus in Environmental Technology: Principles and Applications. Ed. Valsami-Jones E. IWA Publishing, London, UK: 79-92.

Haynes RJ 1982. Effects of liming on phosphate availability in acid soils. Plant and Soil 68: 289-308.

Haynes RJ 1986. Laboratory study of soil acidification and leaching of nutrients from a soil amended with various surface-incorporated acidifying agents. Fertilizer research 10: 165-174.

Haynes RJ, Mokolobate MS 2001. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: a critical review of the phenomenon and the mechanisms involved. Nutrient Cycling in Agroecosystems 59: 47-63.

He Z, Baligar V, Martens D, Ritchey K, Kemper W 1996. Factors affecting phosphate rock dissolution in acid soil amended with liming materials and cellulose. Soil Science Society of America Journal 60: 1596-1601.

Hedley MJ, Stewart JWB, Chauhan BS 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Science Society of America Journal 46: 970-976.

Hendershot WH, Lalande H, Duquette M 1993. Chapter 16: Soil reaction and exchangeable acidity. In: Carter MR ed. Soil sampling and methods of analysis, Lewis Publishers: 141-185.

Hertel TW 2011. The global supply and demand for agricultural land in 2050: A perfect storm in the making? American Journal of Agricultural Economics 93: 259-275.

Hewitt AE 2010. New Zealand soil classification - 3rd edition. Manaaki Whenua Press: 136 p.

Hinsinger P 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. Plant and Soil 237: 173-195.

Hinsinger P, Gilkes RJ 1996. Mobilization of phosphate from phosphate rock and alumina–sorbed phosphate by the roots of ryegrass and clover as related to rhizosphere pH. European Journal of Soil Science 47: 533-544.

Hoagland DR, Arnon DI 1950. The water-culture method for growing plants without soil. California Agricultural Experiment Station Circular 347: 1-32.

Hocking PJ 2001. Organic acids exuded from roots in phosphorus uptake and aluminum tolerance of plants in acid soils. In Advances in Agronomy. Academic Press: 63-97.

Horne DJ, Sojika RE 2002. Aeration, tillage effects on. In: Encyclopedia of Soil Science. Lal, R. ed. New York, Marcel Dekker: 36-39.

Horsnell L. 1985. The growth of improved pastures on acid soils. 1. The effect of superphosphate and lime on soil pH and on the establishment and growth of phalaris and lucerne. Australian Journal of Experimental Agriculture 25: 149-156.

Howarth RE, Chaplin RKC, Goplen BP, Hall JW, Hironaka R, Majak W, Radostits OM 1991. Bloat in cattle. Agriculture Canada Publications. Ottawa, Ontario: 34 p.

Hsu P, Jackson M 1960. Inorganic phosphate transformations by chemical weathering in soils as influenced by pH. Soil Science 90: 16-24.

Hurlbert SH 1984. Pseudoreplication and the design of ecological field experiments. Ecological Monographs 54: 187-211.

Iho A, Laukkanen M 2012. Precision phosphorus management and agricultural phosphorus loading. Ecological Economics 77: 91-102.

Johannessen T, Dahl E 1996. Declines in oxygen concentrations along the Norwegian Skagerrak Coast, 1927-1993: A signal of ecosystem changes due to eutrophication? Limnology and Oceanography 41: 766-778.

Kalbitz K, Geyer W, Geyer S 1999. Spectroscopic properties of dissolved humic substances - a reflection of land use history in a fen area. Biogeochemistry 47: 219–238.

Kalff J 2002a. Inorganic carbon and pH. In Limnology. Ed. Ryu T. Prentice-Hall, Inc, New Jersey: 222-223.

Kalff J 2002b. Temperature cycles, lake stratification, and heat budgets. In Limnology. Ed. Ryu T. Prentice-Hall, Inc, New Jersey: 154-178.

Kasimir-Klemedtsson Å, Klemedtsson L, Berglund K, Martikainen P, Silvola J, Oenema O 1997. Greenhouse gas emissions from farmed Organic soils: a review. Soil Use and Management 13: 245-250.

Khan F, Ansari A 2005. Eutrophication: an ecological vision. The Botanical Review 71: 449-482.

Kleinman P, Sharpley A, Saporito L, Buda A, Bryant R 2009. Application of manure to no-till soils: phosphorus losses by sub-surface and surface pathways. Nutrient Cycling in Agroecosystems 84: 215-227.

Kleinman PA, Sharpley A, McDowell R, Flaten D, Buda A, Tao L, Bergstrom L, Zhu Q 2011. Managing agricultural phosphorus for water quality protection: principles for progress. Plant and Soil 349: 169-182.

Kleinman PJA, Needelman BA, Sharpley AN, McDowell RW 2003. Using soil phosphorus profile data to assess phosphorus leaching potential in manured soils. Soil Science Society of America Journal 67: 215-224.

Kollet SJ, Maxwell RM 2006. Integrated surface–groundwater flow modeling: A free-surface overland flow boundary condition in a parallel groundwater flow model. Advances in Water Resources 29: 945-958.

Kristensen T, Søegaard K, Kristensen IS 2005. Management of grasslands in intensive dairy livestock farming. Livestock Production Science 96: 61-73.

Lal R, Hall GF, Miller FP 1989. Soil degradation: I. Basic processes. Land degradation and development 1: 51-69.

Lambin EF, Meyfroidt P 2011. Global land use change, economic globalization, and the looming land scarcity. Proceedings of the National Academy of Sciences 108: 3465-3472.

Larson GA, Roloff G, Larson WE 1988. A new approach to marginal agricultural land classification. Journal of Soil and Water Conservation 43: 103-106.

Lee CH, Hong CO, Kim SY, Schumacher T, Kim PJ 2011. Reduction of phosphorus release by liming from temporary flooded rice rotational system in greenhouse upland soil. Ecological Engineering 37: 1239-1243.

Lierop WV 1983. Lime requirement determination of acid Organic soils using buffer-pH methods. Canadian Journal of Soil Science 63: 411-423.

Likens GE, Bartsch AF, Lauff GH, Hobbie JE 1971. Nutrients and eutrophication. Science 172: 873-874.

Lindsay WL 1979. Phosphates. In Chemical equilibria in soils. John Wiley and Sons Ltd., Chichester, Sussex: 162-205.

Littleboy M, Smith DM, Bryant MJ 1996. Simulation modelling to determine suitability of agricultural land. Ecological Modelling 86: 219-225.

Lourenzi CR, Ceretta CA, Cerini JB, Ferreira PAA, Lorensini F, Girotto E, Tiecher TL, Schapanski DE, Brunetto G 2014. Available content, surface runoff and leaching of phosphorus forms in a typic hapludalf treated with organic and mineral nutrient sources. Revista Brasileira de Ciência do Solo 38: 544-556.

Lovley DR, Phillips EJP 1986. Organic matter mineralization with reduction of ferric iron in anaerobic sediments. Applied and Environmental Microbiology 51: 683-689.

Lowther WL, Hay RJM, Ryan DL 2012. Effect of strain of rhizobia, lime, and phosphorus on dry matter yield of three lotus species in differing environments in Otago and Southland. New Zealand Journal of Experimental Agriculture 15: 135-142.

Lundström US, van Breemen N, Bain D 2000. The podzolization process. A review. Geoderma 94: 91-107.

Lutz JF, Pinto RA, Garcia-Lagos R, Hilton HG 1966. Effect of phosphorus on some physical properties of soils: II. Water retention. Soil Science Society of America Journal 30: 433-437.

Mack AR, Barber SA 1960. Influence of temperature and moisture on soil phosphorus I. effect on soil phosphorus fractions. Soil Science Society of America Journal 24: 381-385.

MacLeod CJ, Moller H 2006. Intensification and diversification of New Zealand agriculture since 1960: An evaluation of current indicators of land use change. Agriculture, Ecosystems and Environment 115: 201-218.

Majak W, McAllister TA, McCartney D, Stanford K, Cheng KJ 2003. Bloat in cattle. Alberta Agriculture and Rural Development, Edmonton, Alberta. Available on line at: http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/agdex6769. Accessed April 2014).

Mann CC 1999. Crop scientists seek a new revolution. Science 283: 310-314.

Marttila H, Kløve B 2010a. Dynamics of erosion and suspended sediment transport from drained peatland forestry. Journal of Hydrology 388: 414-425.

Marttila H, Kløve B 2010b. Managing runoff, water quality and erosion in peatland forestry by peak runoff control. Ecological Engineering 36: 900-911.

Mataix-Solera J, Doerr SH 2004. Hydrophobicity and aggregate stability in calcareous topsoils from fire-affected pine forests in southeastern Spain. Geoderma 118: 77-88.

McDowell RW, Condron LM, Mahieu N, Brookes P, Poulton P, Sharpley A 2002. Analysis of potentially mobile phosphorus in arable soils using solid state nuclear magnetic resonance. Journal of Environmental Quality 31: 450-456.

McDowell RW 2012. Challenges and opportunities to decrease phosphorus losses from land to water. Advanced Nutrient Management: Gains from the Past-Goals for the Future. (Eds Currie LD, Christensen CL). http://flrc.massey.ac.nz/publications.html. Occasional Report (25).

McDowell RW 2008. Phosphorus in humped and hollowed soils of the Inchbonnie catchment, West Coast, New Zealand: I. Variation with age and distribution. New Zealand Journal of Agricultural Research 51: 299-306.

McDowell RW, Catto W 2005. Alternative fertilisers and management to decrease incidental phosphorus loss. Environmental Chemistry Letters 2: 169-174.

McDowell RW, Condron LM 2004. Estimating phosphorus loss from New Zealand grassland soils. New Zealand Journal of Agricultural Research 47: 137-145.

McDowell RW, Condron LM, Stewart I 2008. An examination of potential extraction methods to assess plant-available organic phosphorus in soil. Biology and Fertility of Soils 44: 707-715.

McDowell RW, Cosgrove GP, Orchiston T, Chrystal J 2014. A cost-effective management practice to decrease phosphorus loss from dairy farms. Journal of environmental quality 43: 2044-2052.

McDowell RW, Larned ST, Houlbrooke DJ 2009. Nitrogen and phosphorus in New Zealand streams and rivers: Control and impact of eutrophication and the influence of land management. New Zealand Journal of Marine and Freshwater Research 43: 985-995.

McDowell RW, Littlejohn RP, Blennerhassett JD 2010. Phosphorus fertilizer form affects phosphorus loss to waterways: a paired catchment study. Soil Use and Management 26: 365-373.

McDowell RW, Monaghan RM 2014. Extreme phosphorus losses in drainage from grazed dairy pastures on marginal land. Journal of Environmental Quality 44: 545-551.

McDowell RW, Monaghan RM, Carey P 2003a. Potential phosphorus losses in overland flow from pastoral soils receiving long-term applications of either superphosphate or reactive phosphate rock. New Zealand Journal of Agricultural Research 46: 329-337.

McDowell RW, Monaghan RM, Morton J 2003b. Soil phosphorus concentrations to minimise potential P loss to surface waters in Southland. New Zealand Journal of Agricultural Research 46: 239-253.

McDowell RW, Nash D 2011.A review of the cost-effectiveness and suitability of mitigation strategies to prevent phosphorus loss from dairy farms in New Zealand and Australia. Journal of Environmental Quality 41: 680-693.

McDowell RW, Nash DM, Robertson F 2007. Sources of phosphorus lost from a grazed pasture receiving simulated rainfall. Journal of Environmental Quality 36: 1281-1288.

McDowell RW, Sharpley AN 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. Journal of Environmental Quality 30:508-520.

McDowell RW, Sharpley AN, Bourke W 2008 Treatment of drainage water with industrial by-products to prevent phosphorus loss from tile-drained land. Journal of Environmental Quality 37: 1575-1582.

McDowell RW, Sharpley AN, Condron LM, Haygarth PM, Brookes PC 2001. Processes controlling soil phosphorus release to runoff and implications for agricultural management. Nutrient Cycling in Agroecosystems 59: 269-284.

McDowell RW, Sinaj S, Sharpley AN, Frossard E 2001. The use of isotopic exchange kinetics to determine phosphorus availability in overland flow and subsurface drainage waters. Soil Science 166: 365-373

McKeague JA, Day JH 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Canadian Journal of Soil Science 46: 13-22.

Meersche KVd, Middelburg JJ, Soetaert K, Rijswijk Pv, Boschker HTS, Heip CHR 2004. Carbon-nitrogen coupling and algal-bacterial interactions during an experimental bloom: modelling a 13C tracer experiment. Limnology and Oceanography 49: 862-878.

Meissner R, Leinweber P, Rupp H, Shenker M, Litaor M, Robinson S, Schlichting A, Koehn J 2008 Mitigation of diffuse phosphorus pollution during rewetting of fen peat soils: a trans-European case study. Water, Air, and Soil Pollution 188: 111-126.

Mengel K 2008. Nutrient potentials. In: Chesworth W ed. Encyclopedia of Soil Science, Springer: 496-497.

Metherell A, Condron L, Eden R 1997. Effects of fertiliser rates and forms on soil phosphorus fractions in a long term trial at Winchmore, New Zealand. In: The 18th International Grasslands Congress, Session 10.

Metson AJ, Blakemore LC, Rhoades DA 1979. Methods for the determination of soil organic carbon: a review, and application to New Zealand soils. NZ Journal of Science 22: 205 -228.

Ministry for the Environment [MfE] 2014. National Policy Statement for Freshwater Management 2014. Available at: http://www.mfe.govt.nz/sites/default/files/media/Fresh%20water/nps-freshwater-management-jul-14.pdf

Mihailović V, Hill GD, Mikić A, Ćupina B, Vasiljević S 2008. White lupin as a forage crop on alkaline soils. In: Lupins for health and wealth. Eds. Palta JA, Berger JB. Fremantle, Western Australia: 79-82.

Miller MH 1979. Contribution of nitrogen and phosphorus to subsurface drainage water from intensively cropped mineral and Organic soils in Ontario. Journal of Environmental Quality 8: 42-48.

Miller SS, Liu J, Allan DL, Menzhuber CJ, Fedorova M, Vance CP 2001. Molecular control of acid phosphatase secretion into the rhizosphere of proteoid roots from phosphorus-stressed white lupin. Plant Physiology 127: 594-606.

Minitab 2010. Minitab statistical software. Release 16.2.2. Minitab, State College, PA.

Minneé EMK, Bluett SJ, Woodward SL, Laboyrie PG 2007. Management of *Lotus corniculatus* under dairy cow grazing. Proceedings of the New Zealand Grassland Association 69: 47-51.

Monaghan RM, de Klein CAM, Muirhead RW 2008. Prioritisation of farm scale remediation efforts for reducing losses of nutrients and faecal indicator organisms to waterways: A case study of New Zealand dairy farming. Journal of Environmental Management 87: 609-622.

Monaghan RM, Semadeni-Davies A, Muirhead RW, Elliot S, Shankar U 2010. Land use and land management risks to water quality in Southland. Report prepared for Environment Southland: 85 p.

Moore PA, Reddy KR, Fisher MM 1998. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. Environmental Quality 27: 1428-1439.

Moore PA, Miller DM 1994. decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. Journal of Environmental Quality 23: 325-330.

Moore TR, Clarkson BR 2007. Dissolved organic carbon in New Zealand peatlands. New Zealand Journal of Marine and Freshwater Research 41: 137-141.

Morton J, McDowell R, Monaghan R, Roberts A 2003. Balancing phosphorus requirements for milk production and water quality. Proceedings of the New Zealand Grasslands Association: 111-115.

Murphy J, Riley J P 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chemica Acta 27: 31-36.

Murphy PNC, Stevens RJ 2010. Lime and gypsum as source measures to decrease phosphorus loss from soils to water. Water, Air, and Soil Pollution 212: 101-111.

Naidu R, Syers JK, Tillman RW, Kirkman JH 1990. Effect of liming and added phosphate on charge characteristics of acid soils. Journal of Soil Science 41: 157-164.

Nash D, Hannah M, Halliwell D, Murdoch C 2000. Factors affecting phosphorus export from a pasture-based grazing system. Journal of Environmental Quality 29: 1160-1166.

Nguyen L, Sukias J 2002. Phosphorus fractions and retention in drainage ditch sediments receiving surface runoff and subsurface drainage from agricultural catchments in the North Island, New Zealand. Agriculture, Ecosystems and Environment 92: 49-69.

Nguyen ML, Sheath GW, Smith CM, Cooper AB 1998. Impact of cattle treading on hill land: 2. Soil physical properties and contaminant runoff. New Zealand Journal of Agricultural Research 41: 279-290.

Nichols DS 1983. Capacity of natural wetlands to remove nutrients from wastewater. Journal Water Pollution Control Federation 55: 495-505.

NIWA 2010. National Institute of Water and Atmospheric Research. High Intensity Rainfall System V3. Available on line at: http://hirds.niwa.co.nz/ (accessed March, 2013).

Nye PH, Ameloko AY 1987. Predicting the rate of dissolution of lime in soil. Journal of Soil Science 38: 641-649.

Oburger E, Jones D, Wenzel W 2011: Phosphorus saturation and pH differentially regulate the efficiency of organic acid anion-mediated P solubilization mechanisms in soil. Plant and Soil 341. 363-382.

O'Connor MB, Longhurst RD, Johnston TJM, Portegys FN 2001. Fertiliser requirements for peat soils in the Waikato region. Proceedings of the New Zealand Grassland Association 63: 47-51.

OECD 2008. Environmental performance of agriculture in OECD countries since 1990.

OECD 2015. OECD Economic Surveys New Zealand June 2015 overview.

Olander L, P, Vitousek P, M 2000. Regulation of soil phosphatase and chitinase activity by N and P availability. Biogeochemistry 49: 175-191.

Olila OG, Reddy KR, Stites DL 1997. Influence of draining on soil phosphorus forms and distribution in a constructed wetland. Ecological Engineering 9: 157-169.

Olsen SR 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Colorado Agricultural Experiment Station Scientific journal series no. 418: 18-19.

Olsen SR, Cole CV, Watanabe FS, Dean LA 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939: 18 p.

Olsen SR, Sommers LE 1982. Phosphorus. In: Page AL ed. Methods of soil analysis. Part 2. Agronomic Monographs 9: 2nd ed. ASA, SSSA. Madison, WI: 403-427.

Osborn JF, Pelishek RE, Krammes JS, Letey J 1964. Soil wettability as a factor in erodibility. Soil Science Society of America Journal 28: 294-295.

Otago Regional Council [ORC] 2014. Water Quality Rules (Plan Change 6A). Available at: http://www.orc.govt.nz/Publications-and-Reports/Regional-Policies-and-Plans/Regional-Plan-Water/Water-Quality-Rules-Plan-Change-6A/

Pant HK, Nair VD, Reddy KR, Graetz DA, Villapando RR 2002. Influence of flooding on phosphorus mobility in manure-impacted soil. Journal of Environmental Quality 4: 1399-1405.

Parent LE, Caron J 1993. Chapter 43: Physical properties of Organic soils. In: Carter MR ed. Soil sampling and methods of analysis, Lewis Publishers: 823 p.

Payne RW, Murray DA, Harding SA, Baird DB, Soutar DM 2011. An introduction to GenStat for Windows (14th Edition). VSN International, Hemel Hempstead, UK.

Pearce AJ 1976. Magnitude and frequency of erosion by Hortonian overland flow. The Journal of Geology 84: 65-80.

Perie C, Ouimet R 2008. Organic carbon, organic matter and bulk density relationships in boreal forest soils. Canadian Journal of Soil Science 88: 315-325.

Perrott K, Sarathchandra S, Dow B 1992. Seasonal and fertilizer effects on the organic cycle and microbial biomass in a hill country soil under pasture. Soil Research 30: 383-394.

Perrott KW, Mansell GP 1989. Effect of fertiliser phosphorus and liming on inorganic and Organic soil phosphorus fractions. New Zealand Journal of Agricultural Research 32: 63-70.

Piccolo A, Mbagwu JSC 1999. Role of hydrophobic components of soil organic matter in soil aggregate stability. Soil Science Society of America Journal 63: 1801-1810.

Pokrovsky OS, Dupré B, Schott J 2005. Fe–Al–organic colloids control of trace elements in peat soil solutions: results of ultrafiltration and dialysis. Aquatic Geochemistry 11: 241-278.

Qin B 2009. Lake eutrophication: Control countermeasures and recycling exploitation. Ecological Engineering 35: 1569-1573.

R Core Team 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL http://www.R-project.org.

Rastogi M, Singh S, Pathak H 2002. Emission of carbon dioxide from soil. Current Science: 82: 510-517.

Reddy KR 1983. Soluble phosphorus release from Organic soils. Agriculture, Ecosystems and Environment 9: 373-382.

Reddy KR, O Connor GA, Gale PM 1998. Phosphorus sorption capacities of wetland soils and stream sediments impacted by dairy effluent. Journal of Environmental Quality 27: 438-4473.

Richardson CJ 1989. Freshwater wetlands: transformers, filters, or sinks. In Freshwater Wetlands and Wildlife Eds. Sharitz RR, Gibbons JW. USDOS Office of Scientific and Technical Information, Oak Ridge, Tennessee: 25-46.

Richardson CJ, Qian S, Craft CB, Qualls RG 1996. Predictive models for phosphorus retention in wetlands. Wetlands Ecology and Management 4: 159-175.

Riise G, Van Hees P, Lundström U, Tau Strand L 2000. Mobility of different size fractions of organic carbon, Al, Fe, Mn and Si in Podzols. Geoderma 94: 237-247.

Risk J 2011. Waituna catchment science gaps - land. Environment Southland Technical Comment. 14th June 2011. File reference 701/13/07. 4 p.

Roberts AH, Morton JD 2009. Fertiliser use on New Zealand dairy farms. Revised edition. Auckland, New Zealand, New Zealand Fertiliser Manufacturers Association: 52 p.

Robertson FA, Nash DM 2008. Phosphorus and nitrogen in soil, plants, and overland flow from sheep-grazed pastures fertilized with different rates of superphosphate. Agriculture, Ecosystems and Environment 126: 195-208.

Robson M, Monaghan RM, McDowell RW 2011. Potential nitrogen and phosphorus losses from farms in the Waituna catchment: sources and mitigation. In Report for Environment Southland. Ed. Muirhead RW. AgResearch, Invermay: 23 p.

Ronkanen A-K, Kløve B 2009. Long-term phosphorus and nitrogen removal processes and preferential flow paths in Northern constructed peatlands. Ecological Engineering 35: 843-855.

Rowarth J, Gillingham A, Tillman R, Syers J 1992. Effect of phosphate fertiliser addition and land slope on soil phosphate fractions. New Zealand Journal of Agricultural Research 35: 321-327.

Rowland AP, Haygarth PM 1997. Determination of total dissolved phosphorus in soil solutions. Journal of Environmental Quality 26: 410-415.

Rupp H, Meissner R, Leinweber P 2004. Effects of extensive land use and re-wetting on diffuse phosphorus pollution in fen areas—results from a case study in the Drömling catchment, Germany. Journal of Plant Nutrition and Soil Science 167: 408-416.

Saunders WMH 1965. Phosphate retention by New Zealand soils and its relationship to free sequioxides, organic matter and other properties. New Zealand Journal of Agricultural Research 8: 30-57.

Scanlon BR, Jolly I, Sophocleous M, Zhang L 2007. Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality. Water Resources Research 43: 18 p.

Schachtman DP, Reid RJ, Ayling SM 1998. Phosphorus uptake by plants: from soil to cell. Plant Physiology 116: 447-453.

Schallenberg M, Larned ST, Hayward S, Arbuckle C 2010. Contrasting effects of managed opening regimes on water quality in two intermittently closed and open coastal lakes. Estuarine, Coastal and Shelf Science 86: 587-597.

Schelde K, de Jonge LW, Kjaergaard C, Laegdsmand M, Rubæk GH 2006. Effects of manure application and plowing on transport of colloids and phosphorus to tile drains. Vadose Zone Journal 5: 445-458.

Schipper LA, McLeod M 2002. Subsidence rates and carbon loss in peat soils following conversion to pasture in the Waikato Region, New Zealand. Soil Use and Management 18: 91-93.

Schneider UA, Havlík P, Schmid E, Valin H, Mosnier A, Obersteiner M, Böttcher H, Skalský R, Balkovič J, Sauer T, Fritz S 2011. Impacts of population growth, economic development, and technical change on global food production and consumption. Agricultural Systems 104: 204-215.

Schwarzel K, Renger M, Sauerbrey R, Wessolek G 2002. Soil physical characteristics of peat soils. Journal of Plant Nutrition and Soil Science 165: 479.

Selby M 1972. The relationships between land use and erosion in the central North Island, New Zealand Journal of Hydrology 11: 73-87.

Sharp EL, Parsons SA, Jefferson B 2006. The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts. Environmental Pollution 140: 436-443.

Sharpley AN, Smith SJ 1989. Mineralization and leaching of phosphorus from soil incubated with surface-applied and incorporated crop residue. Journal of Environmental Quality 18: 101-105.

Sharpley AN 1995. Dependence of runoff phosphorus on extractable soil phosphorus. Journal of Environmental Quality 24: 920-926.

Sharpley AN, Kleinman PJA, Heathwaite AL, Gburek WJ, Folmar GJ, Schmidt JP 2008 Phosphorus loss from an agricultural watershed as a function of storm size. Journal of Environmental Quality 37: 362-368.

Sheath GW 1981. *Lotus penduculatus* - an agricultural plant? Proceedings of the New Zealand Grasslands Association 42: 160-168.

Shen H, Yan X, Zhao M, Zheng S, Wang X 2002. Exudation of organic acids in common bean as related to mobilization of aluminum-and iron-bound phosphates. Environmental and Experimental Botany: 48: 1-9.

Sibanda HM, Young SD 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. Journal of Soil Science 37: 197-204.

Simard RR, Beauchemin S, Haygarth PM 2000. Potential for preferential pathways of phosphorus transport. Journal of Environmental Quality 29: 97-105.

Simmonds BM, McDowell RW, Condron LM, Jowett T 2015. Potential phosphorus losses from Organic and Podzol soils: prediction and the influence of soil physico-chemical properties and management. New Zealand Journal of Agricultural Research 59: 1-11.

Simmonds, BM, McDowell RW, Condron LM 2015. Can low-water solubility phosphorus fertilisers decrease phosphorus leaching losses from an acid peat soil? Soil Use and Management. Article in press.

Sims JT, Simard RR, Joern BC 1998. Phosphorus loss in agricultural drainage: historical perspective and current research. Journal of Environmental Quality 27: 277-293.

Sinaj S, Stamm C, Toor GS, Condron LM, Hendry T, Di HJ, Cameron KC, Frossard E 2002. Phosphorus exchangeability and leaching losses from two grassland soils. Journal of Environmental Quality 31: 319-330.

Sinclair AG, Johnstone PD, Smith LC, Risk WH, O'Connor MB, Roberts AH, Morton JD, Nguyen L, Shannon PW 1993. Effect of reactive phosphate rock on the pH of soil under pasture. New Zealand Journal of Agricultural Research 36: 381-384.

Skjemstad JO, Dalai RC, Barren PP 1986. Spectroscopic investigations of cultivation effects on organic matter of Versitols. Soil Science Society of America Journal 50: 354-359

Smith DR, Moore PA, Jr., Griffis CL, Daniel TC, Edwards DR, Boothe DL 2001.Effects of alum and aluminum chloride on phosphorus runoff from swine manure. Journal of Environmental Quality 30: 992-998.

Smith V 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. Environmental Science and Pollution Research 10: 126-139.

Sorn-Srivichai P, Tillman RW, Syers JK, Cornforth IS 1984. The effect of soil pH on Olsen bicarbonate phosphate values. Journal of the Science of Food and Agriculture 35: 257-264.

Stamm C, Fluhler H, Gachter R, Leuenberger J, Wunderli H 1998. Preferential transport of phosphorus in drained grassland soils. Journal of Environmental Quality 27:515– 522.

Steinfeld H, Gerber P, Wassenaar T, Castel V, Rosales M, de Haan C 2006. Livestock's long shadow: environmental issues and options. Food and Agriculture Organization of the United Nations, Rome.

Stepniewska Z, Borkowska A, Kotowska U 2006. Phosphorus release from peat soils under flooded conditions of the Łeczyńsko-Włodawskie Lake District. International Agrophysics 20: 237-243.

Stevens L, Robertson B 2007. Waituna Lagoon 2007 ecological vulnerability assessment and monitoring recommendations. Wriggle Limited, Nelson, New Zealand. Available at: http://www.es.govt.nz/media/5636/waituna-lagoon-ecological-vulnerability-2007.pdf

Stutter MI, Deeks LK, Billett MF 2005. Transport of conservative and reactive tracers through a naturally structured upland Podzol field lysimeter. Journal of Hydrology 300: 1-19.

Summers R, Smirk D, Karafilis D 1996. Phosphorus retention and leachates from sandy soil amended with bauxite residue (red mud). Soil Research 34: 555-567.

Svanbäck A, Ulén B, Etana A 2014. Mitigation of phosphorus leaching losses via subsurface drains from a cracking marine clay soil. Agriculture, Ecosystems and Environment 184: 124-134.

Tadano T, Ozawa K, Sakai H, Osaki M, Matsui H 1993. Secretion of acid phosphatase by the roots of crop plants under phosphorus-deficient conditions and some properties of the enzyme secreted by lupin roots. Plant and Soil 155-156: 95-98.

Täumer K, Stoffregen H, Wessolek G 2005. Determination of repellency distribution using soil organic matter and water content. Geoderma 125: 107-115.

Thompson RMC, Ryder GR 2003. Waituna Lagoon: summary of existing knowledge and identification of knowledge gaps. Department of Conservation: 37 p.

Toor GS, Condron LM, Di HJ, Cameron KC, Cade-Menun BJ 2003. Characterization of organic phosphorus in leachate from a grassland soil. Soil Biology and Biochemistry 35: 1317-1323.

Topoclimate South 2000. Topoclimate South. Land and climate information for a sustainable future. Topoclimate South Trust, Mataura.

Trolove S, Hedley M, Caradus J, Mackay A 1996. Uptake of phosphorus from different sources by *Lotus pedunculatus* and three genotypes of *Trifolium repens*. 1. Plant yield and phosphate efficiency. Soil Research 34: 1015-1026.

Turner BL, Baxter R, Whitton B A 2003. Nitrogen and phosphorus in soil solutions and drainage streams in Upper Teesdale, northern England: implications of organic compounds for biological nutrient limitation. Science of the Total Environment 314–316: 153-170.

Tuukkanen T, Marttila H, Kløve B 2014. Effect of soil properties on peat erosion and suspended sediment delivery in drained peatlands. Water Resources Research 50: 3523-3535.

van den Brandt HMP, Smit HP 1998. Mineral accounting: the way to combat eutrophication and to achieve the drinking water objective. Environmental Pollution 102: 705-709.

Vlahos S, Summers K, Bell D, Gilkes R 1989. Reducing phosphorus leaching from sandy soils with red mud bauxite processing residues. Soil Research 27: 651-662.

Waghorn GC, Tavendale MH, Woodfield DR 2002. Methanogenesis from forages fed to sheep. Proceedings of the New Zealand Grassland Association 64: 167-171.
Walker T, Syers J 1976. The fate of phosphorus during pedogenesis. Geoderma 15: 1-19.

Watanabe FS, Olsen SR 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Science Society of America Journal 29: 677-678.

Williams C 1971. Reaction of surface-applied superphosphate with soil. I. The fertilizer solution and its initial reaction with soil. Soil Research 9: 83-94.

Wills B, Trainor K, Scott D 2003. Legumes for South Island tussock grassland environments - an evaluation of plant survival and growth at some inland Otago and Canterbury trials. In Proceedings of the New Zealand Grassland Association Ed. Moot DJ. Lincoln University, Christchurch: pp 131-142

Wilson, K. 2011. Groundwater in the Waituna Catchment. In: Technical Comment. Environment Southland. 218/04/12: 28 p.

Withers P, Clay S, Breeze V 2001. Phosphorus transfer in runoff following application of fertilizer, manure, and sewage sludge. Journal of Environmental Quality 30: 180-188.

Wolf B 1999. Chapter 6: Soil pH. In The fertile triangle: The interrelationship of air, water, and nutrients in maximizing soil productivity. Food Products Press, New York: 147-176.

Young S, Townsend R, Swaminathan J, O'Callaghan M 2010. *Serratia entomophila*-coated seed to improve ryegrass establishment in the presence of grass grubs. New Zealand Plant Protection 63: 229-234.

Zak D, Gelbrecht J, Steinberg CEW 2004. Phosphorus retention at the redox interface of peatlands adjacent to surface waters in Northeast Germany. Biogeochemistry 70: 357-368.