The influence of New Zealand native vegetation on rhizosphere chemical concentration and speciation in riparian zones

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Abbreviations

Mha – million hectares

t/yr – tonnes per year

SOM – Soil Organic Matter

Pg – Petagrams (10^{15})

SMC – Soil Moisture Content

GMSC – Gravimetric Soil Moisture Content

SFFP – Silver Ferns Farms Pareora

ANOVA – Analysis of variance

TP – Total Phosphorus

TN – Total Nitrogen

NGO – Non Government Organisation

mg/L – milligram per litre

mL – millilitre

µL – microlitre

MP-AES – Microwave Plasma Atomic Emission Spectrometer

kPa – kilopascal

WHC – Water holding capacity

Abstract

The quality of New Zealand's surface waters has been identified as the most important environmental issue in agricultural landscapes. Waterways are degraded through nitrogen (N), phosphorus (P), sediments and pathogens that enter via stock access to drains, streams and rivers as well as runoff and leaching from adjacent fields. Often, NZ-native vegetation, which is depauperate in agricultural landscapes, is established in riparian zones to improve water quality by intercepting these contaminants before they enter waterways. Such plantings have expensive initial costs; it requires retirement of productive agricultural land, vegetation planting, labour costs and maintenance as well as fencing to prevent stock intrusion into the waterways. However, it is estimated that national-level planting initiatives could yield net benefits of $1.7 billion to $5.2 billion per year. Greenhouse studies have shown that the NZ-native species Mānuka (*Leptospermum scoparium*) and Kānuka (*Kunzea robusta*) affect the N-cycle, and may therefore reduce the flux of N into waterways. This finding indicates that the efficacy of riparian plantings, to reduce contaminant spill over, may be greatly influenced by the species used. I aimed to test the null hypothesis that there is no difference between NZ-native plant species when considering their effect on the concentration and speciation of N, P and other essential nutrients in soils adjacent to waterways. I measured chemical differences in the rhizosphere of *Lolium perenne, Phormium tenax, Kunzea robusta, Leptospermum scoparium, Coprosma robusta* and *Pittosporum eugenioides* at three different locations in New Zealand field conditions. Specifically, in each rhizosphere I measured (1) Soil pH and total C, (2) total N and N-speciation, (3) total P and Olsen-P, (4) Other essential nutrients that may affect the use of vegetation for freshwater protection. I found there were no significant interspecific differences in the rhizosphere concentrations of TN, NO_3^-, NH_4^+, TP and Olsen P under all five NZ-native species. However, TP was affected by cut-and-carry of *Lolium perenne* at SFFP. TS and SO_4^{2-} generally had significantly higher interspecific differences in the rhizosphere concentration of *P. tenax* and *K. robusta* at SFFP and Lake Ellesmere. All other NZ-species showed no significant differences. Soil pH and TC were not significantly influenced by different native species, which could be due to different cycling processes. There was higher Na concentration under *L. perenne* than *P. tenax* at SFFP. This was thought to be from wastewater application onto pasture. The age of plants may be a significant factor in determining interspecific differences in chemical concentrations. Lake Waikare showed no significant interspecific differences in rhizosphere concentrations of chemicals, but the NZ-species planted were less than 2 years of age. The lack of differences does not indicate that NZ-native plant species is not an important consideration for riparian plantings. There are many other potential benefits that specific NZ-species may exhibit, which were not been tested in this study. The selection of NZ-species for riparian plantings should not solely rely on the rhizosphere chemical differences, as found in this research, but should consider ecological and farm management requirements.

1. Introduction

1.1. New Zealand Native plants and agriculture

For the past 85 million years, New Zealand (NZ) native plants have historically depended on soils derived from primary rocks low in essential plant nutrients: soils that are naturally fertile are rare in NZ (Wardle, 1991). This changed in the past two centuries when 45% (12 Mha) of NZ's land area was converted to agriculture and soil fertility was increased through the application of fertilisers and lime (Agricultural and horticultural land use 2018a). Native vegetation covered an estimated 82% of land surface area, before Maori and European settlement (Fleet, 1986). In 2019, the Ministry for Primary industries recorded that native vegetation covered 24% of NZ. Native vegetation has been cleared and converted to productive agriculture pasture. Plants take up nutrients from soil, which must be replaced to maintain soil fertility. Consequently, intensive fertiliser and liming schemes have been introduced to maintain optimal nutrient levels (McLaren and Cameron, 1996; Molloy, 1988). The two most important nutrients in NZ soils through fertilisers are nitrogen (N) and phosphorus (P) (OECD environmental performance review 2017c; Parfitt et al., 2012). In NZ, N fertiliser use has increased 637% from 1990 to 2015 (Stats NZ fertilisers 2019b). The 2017 Organisation for Economic Co-operation and Development (OECD) report stated that NZ had the largest N balance increase of any OECD country, in terms of quantity applied per unit of agricultural land, at 25% from 2000 to 2010 (OECD environmental performance review 2017c). Phosphorus fertiliser use has increased 41% from 1990 to 2015 (Stats NZ fertilisers 2019b). Phosphorus fertiliser use peaked in 2005 at 219,000 tonnes, but has since decreased to 155,000 in 2015 (Stats NZ fertilisers 2019b). Phosphorus fertiliser use per unit area remains among the highest on record in the OECD nations (OECD environmental performance review 2017c). Intensive agricultural systems and urban landscapes degrade adjacent waterbodies (Julian et al., 2017; Larned et al., 2016; Larned et al., 2004; McDowell et al., 2009; McDowell et al., 2013; Parfitt et al., 2012). The 'big' four contaminants responsible for degraded water quality in NZ are N, P, sediments and pathogens. This thesis will not seek to investigate the effects of sediments or pathogens.

A nationwide survey conducted by Cosgrove (2019) indicated that 82% of NZ residents were concerned about the pollution of rivers and lakes. A range of initiatives are being used in the agricultural industry to reduce contaminant leaching to freshwater bodies, including the establishment of riparian buffers (Franklin et al., 2015; Hahner et al., 2014; Marden et al., 2007). Daigneault et al. (2017) estimates that national-level riparian planting initiatives could yield net

benefits of $1.7 billion to $5.2 billion per year. There potentially is a large economic benefit from riparian planting schemes. Diverse native riparian planting also provides many environmental benefits including increased biodiversity and fauna shelter, reduction of soil erosion, carbon sink and moderating stream temperature and light through shading from leaf canopies (Franklin et al., 2015; Pan et al., 2011; Pusey and Arthington, 2003). Plants have been shown to affect nutrient cycling in soil (Figure 1-1) (Dollery et al., 2019; Esperschuetz et al., 2017b; Franklin et al., 2015; Hahner et al., 2014). Nutrients in the form of ions are taken up by plant roots (McLaren and Cameron, 1996). Transpiration is responsible for the convective transport of nutrients towards the roots of plants. As water is transpired from the leaves, roots take up water from the soil as well as some fraction of the dissolved nutrients that this soil moisture contains. When roots take up dissolved nutrients faster than soil moisture (active accumulation), the depleted nutrient is replenished in soil solution through diffusion (Hinsinger et al., 2009). The quantity of nutrients moved is directly related to the mass flow of water (McLaren and Cameron, 1996).

1.2. Plant roots and the mobility of N and P

The rhizosphere is the portion of soil directly surrounding the roots of a plant (Hinsinger et al., 2009). Physical, chemical and biological changes in the rhizosphere can significantly change the synthesis of available nutrients. Plant roots change the conditions in the rhizosphere (Franklin et al., 2015; Hinsinger et al., 2009). As a root grows, some of the outer tissue is removed. This provides a source of organic carbon for microorganisms to feed from. Hence, there is more microbiological activity in the rhizosphere soil than bulk soil. Sloughed off root material as well as root exudates such as organic acids can lead to changes in pH compared to bulk soil. Soil pH affects nutrient solubility and nutrient cycling. Therefore, by changing soil pH, plants may affect the solubility and mobility of N and P, two of the major contaminants in waterways (McLaren and Cameron, 1996). Nitrification is the oxidation process of ammonia (NH_3) to nitrate (NO_3^-), which is available for plant uptake. Different soil chemical properties can change the rate of nitrification in soil. Kyveryga et al. (2004) recorded 89% nitrification of NH_3 to NO_3^- in soils with pH >7.5, whereas only 39% nitrification of NH_3 to NO_3^- in soils with pH <6.0. Sahrawat (1982) evaluated 10 different soils with contrasting pH values and found that soils with a pH from 6.1 to 8.6 formed more NO_3^- than soils with pH <6.0. As well as changing the chemical properties of soil, roots change the physical structure of soil. They can create preferential pathways for water to percolate to groundwater, taking with them dissolved nutrients. Plant foliage may contribute to the net cycle of nutrients within the plant system, if it is not removed for harvesting purposes. The plant canopy increases the quantity of water that is evaporated, therefore reducing the quantity of water fluxes in soil which reduces the total leaching of nutrients. Plant litter will add nutrients and other

chemicals back into the soil (McLaren and Cameron, 1996). This can be avoided if the crop or plant is harvested or removed from the cycle. An example of this would be cut-and-carry processes of ryegrass, like *L. perenne*. All of these properties can change how a plant takes up nutrients from soil. Therefore, riparian plants have the potential to interact with soil nutrients differently, possibly having different properties when protecting freshwater quality of adjacent streams, rivers and lakes. This thesis aims to evaluate how different NZ native vegetation interacts with chemical concentration and speciation compared to adjacent pasture.

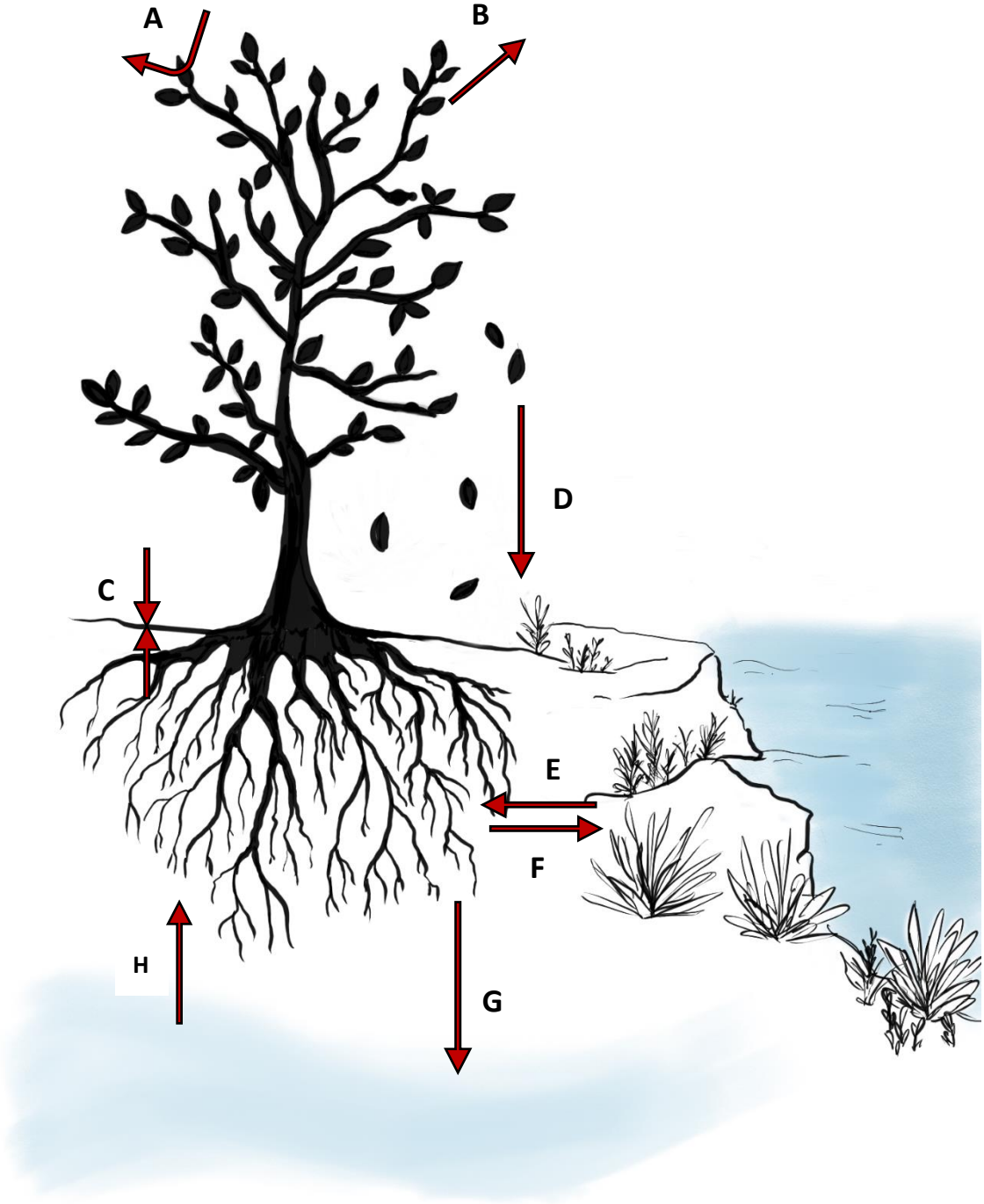


Figure 1-1: Nutrient cycling around the plant-soil interface. A) Evaporation of rainfall from the canopy, reducing water flux through soil. (B) Harvesting of crops removes nutrients from the plant cycle. (C) Roots stabilise the soil, reducing erosion of soil to waterways. (D) Falling leaves decompose in soil, increasing the organic matter and nutrients. Some nutrients may be soluble and susceptible to leaching. (E) Toxic contaminants in soil may inhibit growth of roots. (F) Roots can change soil conditions, which may change speciation of nutrients. (G) Roots create preferential pathways when they create macro pores in soil, which may increase leaching of nutrients to groundwater. (H) Roots take up water from soil through transpiration, convection and concentration gradients. Since water is a transport for soluble nutrients, it reduces leaching if taken up by the plant. Adapted from Robinson et al. 2009

1.3. Previous work

Several studies from 2014 to 2019 in NZ investigated the interactions of NZ native plants with nutrients and contaminants in soil. Most studies have investigated N fluxes, as N is a well-known nutrient to leach from agricultural land. Hahner et al. (2014) found different soil conditions beneath native species and soil planted with shallow-rooted pasture grass (ryegrass). However, they found no difference between soil NO_3^- in the rhizosphere of ryegrass compared to NZ-native species *Phormium tenax, Coprosma robusta and Kunzea robusta.* Franklin et al. (2015) found significant variation in soil mineral N concentrations in the rhizosphere of different native species in pot trials. Native species tolerated high N-loadings, but showed no significant growth response to different N-loadings. They found that native monocots were generally better at sequestering N than native dicots. Dollery et al. (2019) found that native non N-fixing plants more effectively lowered soil NO_3^- concentrations than native N-fixing plants in pot trials. The interaction between pH and N speciation appeared to be important in establishing native vegetation on fertile agricultural soils. The application of Olsen P and lime without N application had little or detrimental effects on plant growth. (Esperschuetz et al., 2017b) found that the addition of urea fertiliser produced a positive growth response from all native vegetation in the experiment. Additionally, *L. scoparium* and *K. robusta* leached lower amounts of NO_3^- (2 kg ha^{-1} NO_3^-) compared to non-native species *P. radiata* (53 kg ha^{-1} NO_3^-). Overall, it seemed that *L. scoparium* and *K. robusta* had similar or better efficacy at reducing nitrification and hence denitrification (N_2O emissions) as they had higher N uptake.

Several studies have investigated the impact of adding biosolids in soil as a fertiliser to assist in native vegetation growth. This elevates N, P and other nutrients as well as contaminants in the soils. This has had different effects on native vegetation. (Esperschuetz et al., 2017a) reported an increase of total dry biomass of Mānuka and Kānuka of 117% and 90%, respectively, after the addition of biosolids (1,250 kg N ha^{-1} equivalent). Biosolids increased the foliage concentrations of N, P and trace elements, suggesting the increase of plant uptake of chemicals. Although foliar concentrations increased, they did not exceed threshold values. Seyedalikhani et al. (2019) found an increase of dried biomass of *L. scoparium* and *K. robusta* of 120% and 170%, respectively, from the addition of biosolids (1,500 kg N ha^{-1} equivalent). Oil production, following biosolids addition, increased by 211%, increasing the economic value of the plants. Although foliar concentrations increased, they did not exceed threshold values.

1.4. Hypothesis/Aims

There is evidence to indicate that there are inter specific differences in NZ native plants, with regards to their effects on chemical fluxes in their rhizospheres. I sought to test the null hypothesis that there is no difference between NZ-native plant species when considering their effect on the concentration and speciation of nitrogen, phosphorus and other essential nutrients in soils adjacent to waterways.

The aim of this thesis is to determine chemical differences in the rhizosphere of *Phormium tenax, Kunzea robusta, Leptospermum scoparium, Coprosma robusta, Pittosporum eugenioides* and *Lolium perenne* (non-native control) that will affect the concentration of nitrogen, phosphorus and other essential nutrients. Specifically, in each rhizosphere I sought to measure:

- (1) Soil pH and total C,
- (2) Total N and N-speciation,
- (3) Total P and Olsen-P,
- (4) The concentration of other elements that may affect the use of the species for waterway protection.

The overarching goal of this research was to provide stakeholders with a broader collection of native riparian planting species that have improved N and P attenuating characteristics. The expectation is that riparian planting initiatives can be planned more effectively and efficiently, if the chemical rhizosphere conditions are better understood, to protect freshwater quality of streams, lakes and rivers adjacent to intensively farmed land.

2. Background

2.1. New Zealand's Freshwater Resources

Freshwater has been an important source of mahinga kai to tangata whenua for generations. Ki uta ki tai (from the mountains to the sea) encompasses the numerous interactions freshwater will have with the surrounding environment as it traverses from the mountains to the sea (Our Fresh Water 2017b). To determine the health of freshwater quality, systematic long-term monitoring of chemical, ecological, physical and biological parameters is required (Ballantine and Davies-Colley, 2014). The National Rivers Water Quality Network (NRWQN) is a monitoring network operated by the National Institute of Water and Atmospheric Research (NIWA). The NRWQN provides reliable scientific data on chemical, physical and biological characteristics. It consists of 77 monitoring sites on 35 rivers across NZ. The National Policy Statement for Freshwater Management (NPS-FM) is the NZ guideline to assist regional councils and communities to plan more efficiently for integrated and sustainable freshwater objectives. The NPS-FM sets national bottom line standards for key scientific parameters, providing a baseline which safeguards freshwater quality (NPS - Freshwater Management 2017a). However, national bottom line standards are not the target to aim for, but merely a foundation to build off towards improved quality. The value of NZ's freshwater resources emerge from the significance humans have for water quality and human wellbeing (Table 2-1). Communities, stakeholders and iwi/hapu have various values and opinions regarding the use of freshwater, which may be conflicting (Gluckman et al., 2017).

Table 2-1: Different values of freshwater ecosystems.

Economic	**Urban**	**Cultural**	**Social/Recreational**	**Environmental**
• Aquaculture • Hydroelectricity • Agricultural • Industrial • Tourism	• Household use • Clean drinking water	• Mahinga Kai • Mauri (life) • Ki uta ki ta (mountains to sea)	• Swimming • Boating • Fishing • Kayaking • Aesthetic	• Biodiversity • Indigenous species • Chemical, physical, biological and ecological factors • Ecosystem services

The NPS-FM sets minimum benchmark values for total N & P, NO_3^-, NH_4^+, dissolved oxygen and *E. coli* that are consistent across NZ. The local community must assist the local council to take responsibility to facilitate the pathway and timeline to ensure minimum benchmarks are not exceeded.

2.1.1. Influence of land to freshwater

An extensive change to land use over the last century has occurred worldwide coinciding with exponential population growth. Human activity has altered atmospheric composition, hydrological cycles and ecosystem habitats (Foley et al., 2005). A major land use change observed in NZ has been the clearing of indigenous forests for agriculture (Fleet, 1986). Agricultural fertilisers for modern day cropping are fundamental to meet the nutritional needs of humans (Bennett et al., 2001; Vitousek et al., 1997). During 2017, NZ used three primary fertilisers that made up 75% of fertiliser use. An estimated 403,000 tonnes of Urea (N-fertiliser), 818,000 tonnes of Superphosphate (P-fertiliser) and 1,020,000 tonnes of Lime were used throughout NZ. This is adding significant quantities of nutrients and contaminants into the environment. There is a well-documented relationship between high-intensity agriculture and urban landscapes adjacent to water bodies causing a decline in freshwater quality (Ballantine and Davies-Colley, 2014; Julian et al., 2017; Larned et al., 2016; Larned et al., 2004; McDowell et al., 2009; McDowell et al., 2013). Cullen et al. (2006) presents four key reasons for water quality coming under increasing pressure, (1) non-point (diffuse) discharges; (2) access to waterways by stock; (3) urban development; and (4) forestry. This study focuses primarily on diffuse discharges to freshwater environments.

2.1.2. Non-point (diffuse) sources of pollution

Non-point source pollution refers to contaminants that enter the catchment through an array of sources, largely from agricultural or urban discharge (Roygard et al., 2012). With heavy rainfall, surface water flow can transport natural and anthropogenic contaminants into rivers, streams, lakes, estuaries and groundwater, thereby degrading freshwater quality (Caruso, 2000). Non-point contaminants move into water bodies through three main processes: (1) surface runoff, (2) direct access of livestock to waters, and (3) leaching of groundwater contaminants (Howard-Williams et al., 2010). The contaminants broadly associated with non-point pollution are fine sediments, pathogens and nutrients (Caruso, 2000; Dillaha et al., 1989; Howard-Williams et al., 2010). Elliott et al. (2005) estimated that point sources (e.g. pipe discharges) in NZ contribute just 3.2% and 1.8% of the TN and TP, respectively, to nutrient fluxes in streams/rivers. The remaining contribution to nutrient fluxes in streams/rivers is assumed to derive from leaching of natural and anthropogenic non-point sources. Howard-Williams et al. 2010 estimate that some 75% of non-point nutrients (N and P) are from modified landscapes, while the remaining 25% is natural, illustrating the large influence non-point pollution has on nutrient fluxes.

2.1.3. Eutrophication

Eutrophication is the process of excessive plant growth in aquatic environments resulting from nutrient enrichment induced by human activity (Smith and Schindler, 2009). The primary drivers of eutrophication in NZ are from excess N and P. These exacerbate the growth of harmful algae (Álvarez et al., 2017) that deoxygenate stratified freshwater lakes (Abell et al., 2010) and release toxins (Larned et al., 2016). The result is damaging physiological stress in fish and loss of pollution-sensitive invertebrates (Larned et al., 2016). Larned et al. (2016) analysed NZ river-water quality and found that water-quality adjacent to pastoral and urban land is generally poorer compared to natural vegetated areas. This was shown by elevated median concentrations of nutrients and *E. coli*. They also found that water-quality at lowland sites was generally poorer than upstream sites. NZ has implemented strategies to reduce the quantities of N and P entering waterways. This includes limits on fertiliser use (MPI Stock Exclusion Reports 2016; Agricultural and horticultural landuse 2018a), reducing stock access to waterways and riparian planting (Stutter et al., 2012a).

2.1.3.1. Management of Nutrients in New Zealand

OVERSEER Nutrient Budgets (Overseer) was designed as a support tool to calculate nutrient flows around localised farm systems. Overseer is used extensively, as it is the primary backbone for decisions regarding farm fertiliser systems in NZ (Shepherd and Wheeler, 2012). In its simplest form, Overseer measures the inputs and diffuse outputs of nutrients across a defined boundary (Wheeler et al., 2003). Quantifying the diffuse outputs of nutrients is challenging, hence the extent of contribution of the deleterious effects of nutrients to surrounding ecosystems can be ambiguous. Overseer integrates decades of applied farm research into local farm scale models (Murray et al., 2016).

2.1.4. Riparian Zones

The riparian zone is the interface between the aquatic and terrestrial environment; inclusive of stream beds, banks and floodplains (Swanson et al., 1982). Riparian zones are regularly referred to as buffer zones, as they contribute significantly to aquatic ecosystem resilience. They are a fundamental habitat for both aquatic and terrestrial species (Pusey and Arthington, 2003; Swanson et al., 1982). Riparian zones are three-dimensional spatial and temporally diverse environments (Lee et al., 2003; Lee et al., 2004). Stutter et al. (2012a) reports that wider riparian buffer zones are more effective in reducing the pressure exerted from adjacent farmland on aquatic ecosystems. However, a wider buffer zone is more expensive, which incentivises cost-effective riparian zones. Parkyn et al. (2000) recommended a

vegetation buffer width of >10 m for urban environments to develop a self-sustaining, indigenous vegetation strip that will achieve most aquatic functions. However, each unique situation should be treated as an individual case as to fulfil the specific aims and outcomes for that local environment. Below is a table of benefits that riparian zones bring to ecosystems (Table 2-2).

Table 2-2: Benefits of riparian planting to the surrounding freshwater environments.

Benefit	Result	Reference
Shading, moderating stream temperature and light	Riparian canopy regulates the transfer of thermal energy to aquatic ecosystems.	(Pusey and Arthington, 2003)
Woody debris	A habitat for fish, invertebrates & microalgae. Important for bird life.	(Everett and Ruiz, 1993) (Crook and Robertson, 1999)
Reduction in soil erosion	Root systems hold soil in place, resulting in less soil erosion by wind and water processes. Retaining the depth of fertile topsoil.	(Lovell and Sullivan, 2006) (Stutter et al., 2012a)
Food source	Debris and organic material can be a food source for both aquatic and terrestrial biota.	(Kuglerová et al., 2014)
Carbon Sink	Riparian plants can be carbon sinks, absorbing carbon from the atmosphere and surrounding soil.	(Pan et al., 2011)
Contaminant Runoff	Can assist in removing nutrients, pesticides and/or pathogens. But in saturated conditions, this reduces their effectiveness.	(Radkins Jr et al., 1998) (Magette et al., 1989) (Lee et al., 2003) (Stone et al., 2004) (Kovacic et al., 2000)

Renouf and Harding (2015) characterised the width and vegetation composition of riparian zones in Canterbury. Some 65% of riparian zones surveyed were <5 m. Exotic plant species were present at 99% of sites and dominant at 81% of sites. Exotic willows and poplars were the most common exotic trees, as they were extensively used for river protection and bank stability from the 1930's (Marden et al., 2007; Phillips, 2005). *P. tenax* and native sedges (e.g. *Carex secta)* were the most abundant native species, present at 34% of sites and dominant at 14%. There were no other native species dominant in a riparian zone. Greenwood et al. (2012) found riparian buffers were on average <5 m wide and dominated by exotic weeds and/or shrubs. However, they found adequate stock exclusion from waterways, most of which were either fenced or had natural barriers that limited access. Most

riparian zones in Canterbury are less than adequate for effective nutrient management (Parkyn et al., 2000). They lack the diversity of tree species to cope with the changes of land use activity and intensity (Renouf and Harding, 2015). There is a large upfront cost associated with riparian planting. A planting model with plants at 1.5 metre spacing and a planting density of 4500 plants per hectare, would cost an estimated NZ$3.67 per linear metre for a combination of native flax and sedge/grass (MPI Stock exclusion costs report 2016). Assuming these numbers, to plant a riparian zone that is 500 metres long and with a buffer width of 15 metres, it would cost an estimated NZ$150,000. There would also be additional ongoing costs for maintenance and profits lost due to less available land for primary production.

2.1.5. Historic Vegetation Cover in New Zealand

New Zealand's indigenous forests, before Maori and European settlement, was estimated to cover 82% of the land surface area in NZ (Fleet, 1986). The Ministry for Primary Industries record that indigenous forests now cover just 24%, a total loss of some 14 million ha of land. The greatest loss has occurred on the east coast of the South Island and the lower North Island (Ewers et al., 2006). Most deforested land has been converted into urban, horticultural or agricultural land (Ewers et al., 2006). Large-scale clearance of forested areas began in the 1870s. Early European settlers were required by law to improve their land. This resulted in extensive burning of indigenous forests, which freed land for the expansion exotic grasses. Proce et al. (2006) recorded 31% was legally protected land in 2005. This indicates an upward trend for the protection of indigenous land area cover. Cieraad et al. (2015) recorded that 35.3% of NZ land in 2012 was legally protected for natural heritage purposes. NZ has set the goal to plant one billion trees before 2028. As of May 18th 2020, nearly 150 million trees have been planted (One billion trees programme 2020). Although, only 12% of the trees planted are native.

2.2. Importance of nutrients for plants

Most nutrients required for plant growth are taken up from soil. Therefore, roots have the potential to intercept nutrient fluxes from adjacent agricultural land and protect freshwater quality (Stone et al., 2004; Stutter et al., 2012a). Plants interact with the chemicals in soil, from both natural and anthropogenic sources. Essential nutrients are by definition, elements needed by a plant to complete their life cycle (Fageria, 2016). These elements are not replaceable and are directly involved in plant metabolism processes (Fageria, 2016; McLaren and Cameron, 1996). There are 17 essential elements required for optimal growth and development. These are carbon (C), hydrogen (H), oxygen (O),

nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), boron (B), molybdenum (Mo), chlorine (Cl) and nickel (Ni) (Fageria 2009). Most elements are taken up from the soil, apart from C, H and O, which are atmospherically sourced. Based on the average quantities recorded in plants, elements are categorised as either micronutrients or macronutrients (McLaren and Cameron, 1996). Micronutrients are required in smaller quantities than macronutrients. Some 2-10% of plant biomass is composed of mineral nutrients. The remaining biomass is composed of non-essential nutrients, organic compounds and water (Jobbágy and Jackson, 2004; McLaren and Cameron, 1996). Nutrient concentrations in soils are an indicator of the soil fertility within the agricultural industry.

2.2.1. Nutrient availability

Nutrients undergo several processes in the soil before being absorbed by the plant. All processes are influenced by climate, soil, plant species and location (Fageria, 2016). Plants take up nutrients in ionic form (McLaren and Cameron, 1996). However, for most nutrients in soil, ions only make up a small fraction of the total nutrient. The bulk of the nutrients are commonly fixed in soil organic matrices or adsorbed to soil colloids (Ghani et al., 1991). Physical, chemical and biological changes in the rhizosphere of plants can significantly change synthesis of available nutrients (Franklin et al., 2015). As a root grows, some of the outer tissue is shed. This can provide a rich source of carbon for microorganisms. This can lead to changes in pH and moisture compared to bulk soil, hence significant changes in the availability of nutrients (Fageria, 2016; McLaren and Cameron, 1996).

2.2.2. Nutrient cycling in the soil – plant system

In natural environments, plants return essential elements back to the soil through foliage that undergoes decomposition (Jobbágy and Jackson, 2004). Nutrient cycling is the term used to define this mechanism. Deep-rooted plants draw nutrients from lower soil depths. Nutrients are then concentrated in the top soil as nutrient cycling takes place (McLaren and Cameron, 1996). When the natural vegetation of an environment is removed, this process ceases. Overtime, the soil loses fertility as nutrients are not being replaced. Fertilisers are the primary method for replenishing essential nutrients in intensively worked soils (McLaren and Cameron, 1996). The two elements most replenished by agricultural fertilisers in NZ are N and P (OECD Environmental Performance Review 2017c; Parfitt et al., 2013; Parfitt et al., 2012).

2.3. Nitrogen

2.3.1. From natural to anthropogenic

Nitrogen is the fourth most abundant element Earth's crust (McLaren and Cameron, 1996). It is a primary constituent of amino acids, proteins, enzymes and nucleic acids (McLaren and Cameron, 1996; Stein and Klotz, 2016). It is essential for life and fundamental for successful agricultural processes. The Haber-Bosch process, developed in 1909, quadrupled productivity of N worldwide by industrially converting atmospheric inert dinitrogen gas (N_2) to NH_3. This was the beginning of agricultural intensification from anthropogenic nutrients inputs. Anthropogenic N is now the dominant source of N for most agricultural systems (Stein and Klotz, 2016).

2.3.2. Sources of nitrogen in soil

Nitrogen in the soil is present in three primary forms: (1) organic compounds, (2) NH_4^+ and, (3) NO_3^-. More than 95% of total N in soil is found in organic compounds, which are unavailable for plant uptake. NH_4^+ and NO_3^- are available for plant uptake (McLaren and Cameron, 1996) (Figure 2-1). Until the late 1980s, agricultural production in NZ depended on biological N fixation. *Trifolium repens* (White clover), an N-fixer in the *Fabaceae* family, was the introduced species that held the backbone of NZ's successful agricultural economy (Caradus and Hay, 1989). *Rhizobium* bacteria form nodules on *T. repens* clover roots. The nodules capture atmospheric N, which plants take up. In return, *T. repens* provides carbohydrates for *Rhizobium* bacteria, forming a symbiotic relationship (Bouwman et al., 2009; Ledgard and Steele, 1992). Optimal soil and environmental conditions were required when introducing *T. repens* to NZ (Ledgard and Steele, 1992).

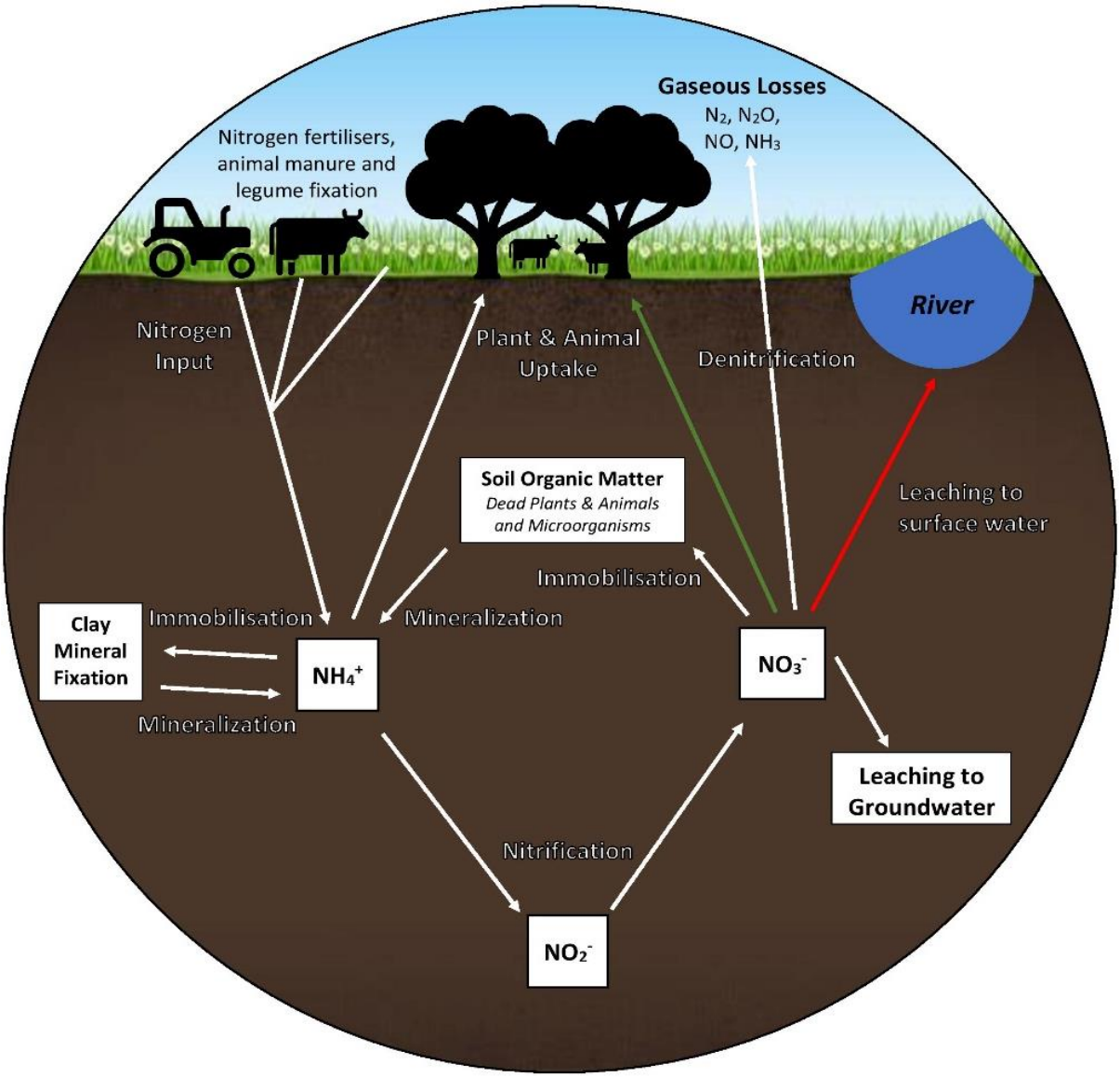


Figure 2-1: An overview of the Nitrogen Cycle in soil. Specifically the above and below-ground transformations of nitrogen. This includes the input sources and losses.

Adapted from McLaren & Cameron (1996).

Since the 1980's, NZ has widely accepted the use of N fertilisers. N-fixation from legumes, such as *T. repens*, diminishes with increased fertiliser input (Parfitt et al., 2012). This has increased NZ's dependence on N fertilisers for agricultural production. From 1985 to 2015, N fertilisers increased from 25,000 t/yr to some 430,000 t/yr, respectively (Stats NZ - Nitrogen and Phosphorus fertilisers 2019b; Parfitt et al., 2012). Urea, in the form of $CO(NH_2)_2$ is the primary N fertiliser used in NZ, contributing 85 % of the total N applied to land via fertilisers (Stats NZ - Nitrogen and Phosphorus fertilisers 2019b). The 2017 Organisation for Economic Co-operation and Development (OECD) report stated that NZ had a 25% increase in N balance per unit of agricultural land, from 2000-2010. The largest N balance increase of any OECD country during this period (OECD environmental performance review 2017c).

2.3.3. Total Nitrogen and Total Carbon

Soil organic matter (SOM) is mainly composed of total nitrogen (TN) and total carbon (TC) as well as other essential nutrients (Batjes, 1996). The quantities of TN and TC are strongly correlated in soil. SOM levels range from 3 % to 20 %, depending on environmental factors such as climate, soil acidity, drainage, soil parent material, human activity and the carbon cycle (McLaren and Cameron, 1996). Soil microbes interact with SOM during cycling processes (Piwpuan et al., 2013). Soils contain between 0.1 % and 0.3 % TN in the top 15 cm of soil (McLaren and Cameron, 1996). The soil is the largest terrestrial pool of TC, with an estimated 1600 Pg of C (Batjes, 1996). The C:N ratio is used as a guide to evaluate the ease of decomposition or mineralisation of nutrients from organic residues. This is useful for planning fertiliser-use within a farm system, as it helps govern how well a certain crop is expected to grow. For most soils, the C:N ratio ranges between 16:1 and 4:1 (McLaren and Cameron, 1996). Organic matter is often most concentrated in topsoil, where plant roots are also most concentrated. Fertilisers increase the concentration of N in topsoil (McLaren and Cameron, 1996; Parfitt et al., 2012).

2.3.4. Nitrification

In soil, dissolved ammonia ($NH_{3\,(aq)}$) is in equilibrium with NH_4^+, which is a function of pH (Beeckman et al., 2018). Nitrification is the oxidation reaction of NH_4^+ to NO_3^-. This is primarily a two-step process. Firstly, ammonia-oxidising bacteria and ammonia-oxidising archaea convert NH_4^+ to NO_2^- (Eq. 2-1). Nitrite-oxidising bacteria convert NO_2^- to NO_3^- (Eq. 2-2) (Stein and Klotz, 2016).

$$2\mathrm{NH}_4^+ + 3\mathrm{O}_2 \rightarrow 2\mathrm{NO}_2^- + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{H}^+ + \text{energy} \qquad (2\text{-}1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \quad (2\text{-}2)$$

Nitrite, under most soil conditions, rapidly converts to NO_3^-. This is a favourable reaction for plants, as NO_2^- is toxic and may inhibit plant growth. With a high NH_4^+ concentration and soil pH >7.0, NO_2^- will accumulate, as nitrifying bacteria are more likely to be inhibited (Burns et al., 1996). However, this phenomenon is rare, as the oxidation of NH_4^+ acidifies the soil (Eq. 1.1). A third mechanism, discovered in 2015, completes the nitrification reaction in only one step, from NH_4^+ to NO_3^- directly. Instead of bacteria or archaea that oxidise ammonia, the process is controlled by microorganisms called commamox (Stein and Klotz, 2016; Van Kessel et al., 2015). The reaction requires specific soil conditions, which are still being characterised. In general, nitrification will be supported by bacteria and archaea in a two-stage reaction, in which ammonia is oxidised, as described in equations 2-1 and 2-2.

Nitrification is an essential soil mechanism as it regulates the efficiency for vegetation and crops in agricultural processes to use N. Several physical and chemical factors increase or decrease the rate of nitrification and are needed to improve agricultural production. Important physical factors include moisture content, oxygen availability and temperature (Haynes, 1986; Kyveryga et al., 2004; McLaren and Cameron, 1996; Vitousek et al., 1997). A saturated water column fills soil pores with water, reducing the available oxygen for nitrification (Sahrawat, 2008). Therefore oxidation of NH_4^+ will not proceed as readily. McLaren and Cameron (1996) & Haynes (1986) reported that the optimal temperature for nitrification ranges from 25 °C to 35 °C. Nitrification ceases when the temperature is <5 °C and >40 °C (McLaren and Cameron, 1996). The microorganisms responsible for supporting the nitrification reaction require different temperature profiles, to achieve optimal nitrification rates. This temperature is often directly related to their localised climate, as microorganisms can adapt weather patterns (Taylor et al., 2017). Important chemical factors include pH, C:N ratio, abundance of NH_4^+ ions and abundance of nitrifying bacteria and/or archaea. The optimal pH for nitrification ranges from 5.5 to 9.0 (Kyveryga et al., 2004; McLaren and Cameron, 1996; Sahrawat, 1982; Sahrawat, 2008). In acidic soils, nitrification may be inhibited by Al toxicity. In alkaline soils, toxic levels of NH_3 may be present, which can limit oxidising bacteria and archaea (McLaren and Cameron, 1996). High soil C:N ratios will immobilise NH_4^+. With less NH_4^+ ions, there is reduced nitrification (Sahrawat, 2008). An abundance of NH_4^+ and nitrifying archaea or bacteria will maintain high nitrification rates.

2.3.5. Nitrogen soil losses

2.3.5.1. Denitrification

Denitrification is the reduction reaction of NO_3^- or NO_2 to the gases nitric oxide (NO), nitrous oxide (N_2O) and N_2 (Groffman et al., 2006). Luo et al. (1999) reported that denitrification in soil is promoted by key physicochemical factors, such as high soil moisture, high soil temperature, a reduced rate of oxygen diffusion into soil and the presence of reducing N (i.e. NO_3^- or NO_2^-). Spatial and temporal variations in physicochemical factors at local, regional and national scales will influence the rate of denitrification in soil. For example, Serca et al. (1994) estimated the emission rate of N_2O in a Congo Rainforest to be 2.9 kg N_2O-N ha^{-1} yr^{-1}. Hall et al. (2004) estimated the emission rate in a Malaysian Rainforest to be 1.15 kg N_2O-N ha^{-1} yr^{-1}. Choudhary et al. (2002) estimated the emission rate in a NZ tilled agricultural field to be 9.2 kg N_2O-N ha^{-1} yr^{-1}.

Denitrification in soils is estimated to contribute 56% – 70% of N_2O emissions globally. Total emissions of N_2O have increased 19% since pre-industrial times (Saggar et al., 2004). N_2O is a significant greenhouse gas (GHG), with a global warming potential some 298 times greater than that of CO_2. To make matters worse, N_2O also degrades ozone (Butterbach-Bahl et al., 2013; Wrage et al., 2001). Forster et al. (2007) estimated that N_2O emissions from anthropogenic influences quantify to 45% of the total N_2O emissions globally. After N fertiliser has been applied, a higher N_2O:N_2 ratio is observed. There is a higher rate of N_2O volatilisation directly after fertiliser application (Dalal and Allen, 2008). Within a number of days, N_2O volatilisation will slow while N_2 production increases (Letey et al., 1980).

2.3.5.2. Leaching

Most soils have a larger cation exchange capacity (CEC) than anion exchange capacity (AEC). The exception is allophanic soils, which have a high AEC. The CEC and AEC of a soil is the quantitative measure of a soil's ability to hold exchangeable cations or anions, respectively (McLaren and Cameron, 1996). Sparling and Schipper (2002) found the CEC ranged from 4 to 69 cmol cm^{-3} across a range of NZ soil profiles. The CEC in NZ topsoil is often highly correlated to the organic content. A CEC is a prerequisite for farmers to test for before applying fertiliser, as this gives an indication of how the soil will store the fertiliser. NH_4^+ are immobilised on negative exchange sites and may bind. Nitrate is more mobile in soil than NH_4^+, due to its negative charge, repelling it from cation exchange sites (Beeckman et al., 2018; McLaren and Cameron, 1996). Hence, NO_3^- has higher leaching rates than NH_4^+. Leaching rates of NO_3^- depends on concentration, plant N uptake, soil moisture content, soil composition and soil structure (McLaren and Cameron, 1996; Rao and Puttanna, 2000). Up to half of the available N

may be lost in soil before plant uptake (Beeckman et al., 2018). NO_3^- that has leached is not available for plant uptake, reducing the efficiency of the fertiliser. Leached NO_3^- can promote eutrophication in aquatic environments (Abell et al., 2010; Álvarez et al., 2017; Beeckman et al., 2018; McDowell et al., 2009; Parfitt et al., 2012; Smith et al., 2006; Smith and Schindler, 2009). This can cause significant adverse health effects to native fauna and flora (Abell et al., 2010; McDowell et al., 2009; McDowell and Nash, 2012; Parfitt et al., 2012).

2.4. Phosphorus

2.4.1. From natural to anthropogenic

Phosphorus is a key nutrient for growth of pasture and crops. It helps the metabolism of carbohydrates and assists storage and/or transfer of energy from photosynthesis (McLaren and Cameron, 1996). Total P in bulk soil ranges from 0.02 % to 0.15 %, depending on the parent material, weathering process and leaching rates. Natural weathering processes cause minerals high in P, known as apatites, to release P in soil. Tricalcium phosphates ($Ca_3(PO_4)_2$) account for 35%-70% of total soil P (Shen et al., 2011). Historically, agricultural production relied on the weathering of P minerals. However, this is a timely process and with the increasing demand for more productive agricultural processes, P fertilisers have been widely introduced. Figure 2-2 describes the soil P cycle in a grazed pasture.

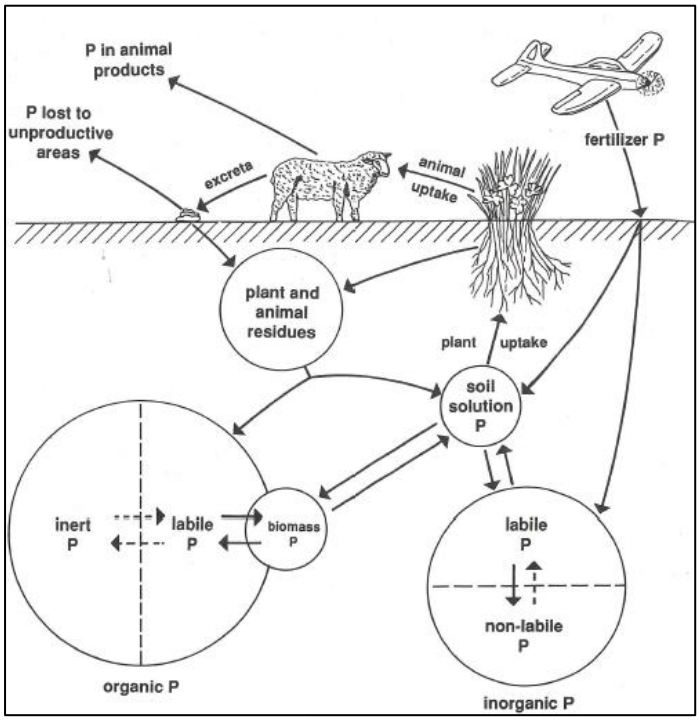


Figure 2-2: An overview of the phosphorus cycle in a grazed pasture. This includes the input sources and losses.

Adapted from McLaren & Cameron 1996

2.4.2. Sources of phosphorus in soil for plants

Weathering of apatite minerals liberates P and consequently P can be: adsorbed by plants, incorporated into the soil organic matter or redeposited as insoluble mineral forms and occluded. With the demand for intensive agriculture and the need for P in crop propagation, P fertilisers are the primary source of plant available P in NZ agricultural processes (Gillingham and Thorrold, 2000). Phosphorite, a sedimentary rock naturally high with P, is the primary constituent of many phosphate (PO_4^{2-}) fertilisers. However, phosphorite rock by itself is composed of insoluble tricalcium phosphates. Sulphuric acid or phosphoric acid must be added to obtain soluble superphosphate or triple superphosphate fertilisers (Eq. 2-3 to 2-5) (Dawson and Hilton, 2011; McLaren and Cameron, 1996).

Superphosphate:

$$2Ca_3(PO_4)_2 + 6H_2SO_4 \rightarrow 4H_3PO_4 + 6CaSO_4 \quad (2\text{-}3)$$

Or

$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2H_2O \quad (2\text{-}4)$$

Triple Superphosphate:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2 \quad (2\text{-}5)$$

Monocalcium phosphate ($Ca(H_2PO_4)_2$) and dicalcium phosphate (Ca_2HPO_4) are the primary forms of soluble PO_4^{2-}. Soluble forms of P are important, as these are available to plants where insoluble are not (McLaren and Cameron, 1996). However, there are two issues with extracting PO_4^{2-} from phosphorite rock. Firstly, phosphorite rock is a limited resource that is only estimated to last another 100 to 400 years (Dawson and Hilton, 2011; Scholz et al., 2013; Schröder et al., 2011). This finite resource is under threat and a suitable renewable option is required for future sustainability. Secondly, the quality of PO_4^{2-} ore has been declining. There has been a decrease in the amount of average PO_4^{2-} that can be extracted from a given amount of phosphorite (Dawson and Hilton, 2011). Plants take P up through their roots in the form of phosphate ions (i.e. $H_2PO_4^-$ and HPO_4^{2-}) (McLaren and Cameron, 1996). There are three primary factors that control the equilibria of plant available P, (1) pH, (2) concentration of competing anions with P ions for ligand exchange, and (3) concentration of metals that adsorb or precipitate out P ions. The most significant condition in soil that influences speciation of PO_4^{2-} ions is pH (Figure 2-3).

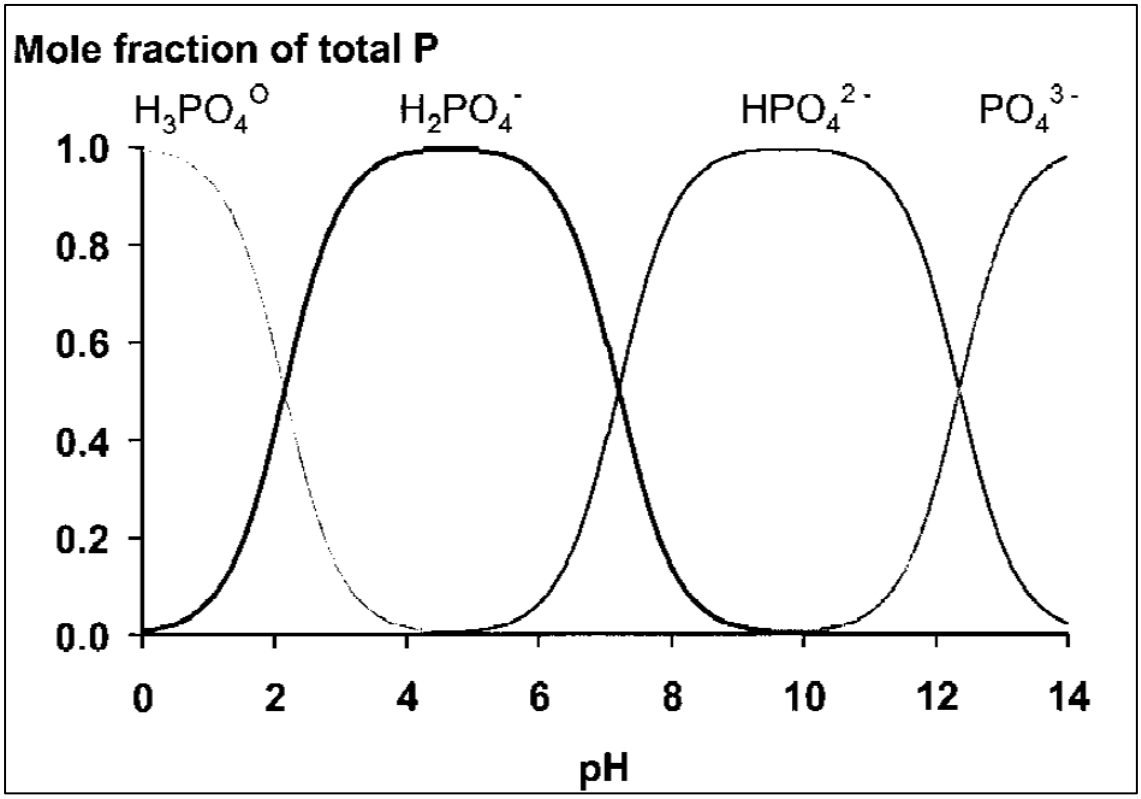


Figure 2-3: Speciation of different phosphate ions at a range of pH levels.

Adapted from Hinsinger. 2001

2.4.3. Phosphorus soil losses

2.4.3.1. Phosphate fixation

Phosphate fixation reduces PO_4^{2-} availability in soil (McLaren and Cameron, 1996; Mengel, 1997). It is one of the four primary mechanisms of soil P loss (Ward et al., 1985). The other three primary losses of soil P are: (1) embodied P in vegetation removed from the farm, (2) animal transfer of P and (3) P lost via water runoff and erosion. There are two key mechanisms responsible for PO_4^{2-} fixation: (1) the formation of less soluble calcium phosphates, and (2) adsorption of soluble PO_4^{2-} to soil particles (Mengel, 1997). McLaren and Cameron (1996), Mengel (1997) & Hinsinger (2001) all report that PO_4^{2-} adsorption to soil particles reduces the availability of PO_4^{2-} at higher rates than PO_4^{2-} forming less soluble $Ca(H_2PO_4)_2$ or Ca_2HPO_4. Up to 75% of plant available P from fertilizers may undergo PO_4^{2-} fixation (McLaren and Cameron, 1996; Stutter et al., 2012b). Leaching rates of PO_4^{2-} are low, due to the strong absorbing potential with metal colloids in soil. Leaching rates are so small that they are often looked at over a geological timescale and not a yearly event (McLaren and Cameron, 1996). Therefore, leaching rates of PO_4^{2-} are negligible.

Metal oxides (notably Iron (Fe) and Aluminium (Al) oxides) sorb PO_4^{2-} ions via ligand exchange reactions on the surface of soil particles (Hinsinger, 2001). Phosphate anions exchange with hydroxide (OH^-) ligands on metal oxides, forming a mononuclear bond. Phosphate is deprotonated and binds to a second OH^- ligand, forming a binuclear bond, thermodynamically more stable than the mononuclear bond (Mengel 1997) (Figure 2-4).

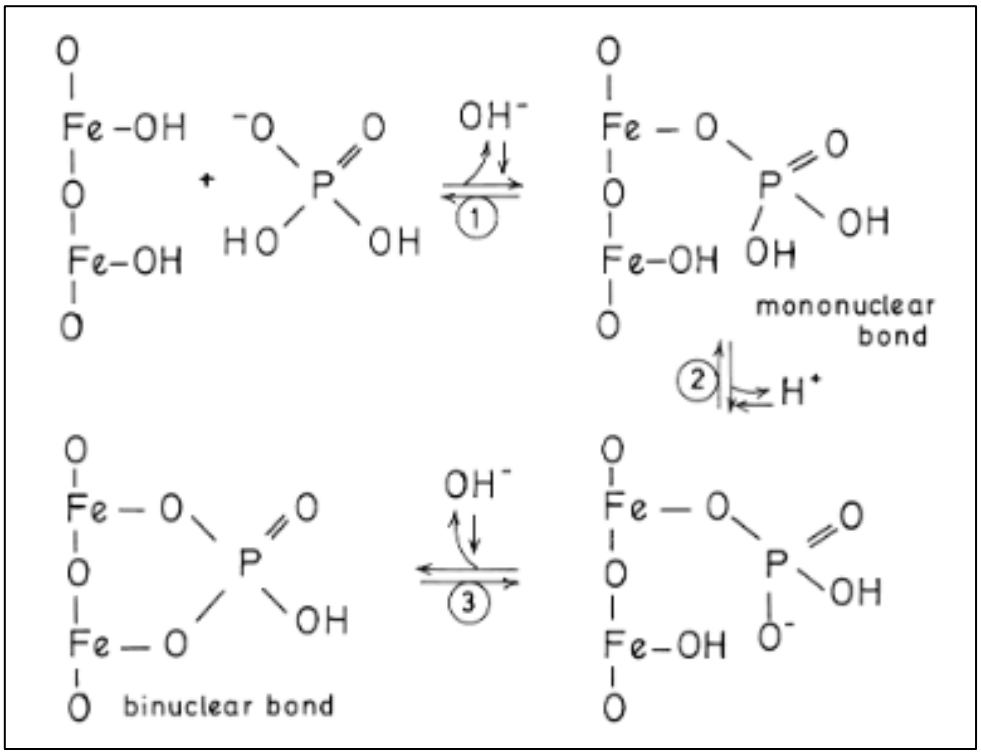


Figure 2-4: Primary method of phosphate adsorption onto adsorbing surface. (1) Ligand exchange reaction of OH^- and phosphate. (2) Deprotonation of monobound phosphate. (3) Second ligand exchange reaction with deprotonated phosphate and OH^- to form a binuclear bond.

Adapted from Mengel et al. 1997

Occlusion is the process of Fe or Al oxides coating adsorbed PO_4^{2-}. This makes PO_4^{2-} ions even less available for plant uptake (McLaren and Cameron, 1996). Acidic soils promote better adsorption of PO_4^{2-} ions to soil particles, reducing in mobility of P (Hinsinger, 2001). Soil pH is the most significant factor in determining the concentration of Fe or Al colloids in soil, which then influences the rate of adsorption from PO_4^{2-}.

2.4.3.2. Runoff and soil erosion

Runoff and soil erosion are two primary pathways for P loss in agricultural landscapes. This can lead to a decline of freshwater quality (McLaren and Cameron, 1996). Runoff is the process of overland water flow into freshwater environments due to a saturated soil column. Runoff may occur in a storm event, where soil moisture capacity has reached a maximum and the result is overland flow of rainfall. Soil erosion is a natural process that occurs as a result of change to the flow regime and sediment supply (Hughes, 2016). A large increase to flow regime (e.g. a storm event) will carry with it a large pool of sediment. Soil-bound P is released in large quantities to aquatic environments when soil erosion is high (McLaren and Cameron, 1996; Withers and Jarvie, 2008). Vegetation increases soil stability, which lowers the rate of soil erosion. When vegetation is removed from riparian zones, the subsequent effect is an increase of erosion (Magette et al., 1989).

2.5. Sediments & Pathogens

2.5.1. Sediments

The transport of sediments to aquatic environments is an important pathway to global geochemical cycles and an integral component to habitat and ecological health (Kemp et al., 2011). Soil erosion is a natural process that occurs as a result of change to the flow regime and sediment supply (Hughes, 2016). Anthropogenic soil erosion increases the sediment loads in water bodies. Human activities such as agriculture, deforestation, mining and urbanization have increased sediment loading to adjacent freshwater bodies (Owens et al., 2005). Sediments can transport soil-bound nutrients, trace elements, pathogens and other toxic chemicals that may cause adverse effects to freshwater quality. Sediments may adversely affect key components of the food chain, by reducing the photosynthetic processes. High sediment loading can cause high turbidity, blocking light and therefore limiting photosynthesis (Kemp et al., 2011). This reduces plankton growth, which decreases invertebrate diversity and count. This causes significant adverse effects on fish communities (Kemp et al., 2011). NZ has relatively high erosion rates, with an estimated 200 megatonnes of suspended sediment delivered to the ocean annually, contributing 1.7% of global ocean sediment delivery (Hicks et al., 2011). There are four main processes that increase erosion of stream banks: (1) changes to catchment hydrology, (2) removal of natural riparian planting, (3) direct stream channel modification and (4), unrestricted livestock access to streams (Hughes, 2016). Riparian vegetation provides bank stability to reduce soil erosion and may uptake plant available nutrients (Aye et al., 2006; Withers and Jarvie, 2008). However, plants may return nutrients back via plant matter decomposition. Vegetation has varying bank stability

properties, depending on the root structure, size and distribution. Planning the species selection and variety for planting initiatives are essential for maintaining soil erosion rates (Withers and Jarvie, 2008). Modelling of soil erosion is an effective way to manage nutrient losses. For more accurate model predictions, key knowledge such as volume water discharge, water quality and local expert knowledge are essential (Farkas et al., 2013). Modelling is widely used for NZ farm management. This provides better decision making for farm systems to prevent soil erosion.

2.5.2. Pathogens

Pathogens or other infectious contaminants are biological agents that arise from faecal contamination. This can cause diseases or illness to its host (NIWA - Infectious Substances2019a). Faecal contamination sources are widespread and diverse but may derive from point sources such as wastewater from sewage plants and animal processing plants. Pathogens may enter freshwater surfaces from direct contact by domestic or uncultivated animals, if appropriate fencing schemes have not been established (Collins et al., 2007). However, even with fencing, diffuse sources of faecal contamination pathways may contaminate freshwater surfaces from surface runoff or subsurface flow through soil (Collins et al., 2007). This is a problem in NZ, as every year over one million New Zealanders participate in swimming in aquatic environments (Claridge et al., 2015). Freshwater contaminated with pathogens increases the risk of gastrointestinal illnesses as well as non-enteric infections such as rashes, eye and ear irritations and infected cuts (Soller et al., 2010). However, regional councils have monitoring programmes for *E. coli* at popular swimming sites to protect the public from pathogen exposure. NZ has set guidelines values for *E. coli* levels based on the quantitative microbial risk assessment for campilobacteriosis (Julian et al., 2017). If guidelines are exceeded, swimmers are advised to stay away. Regional councils will mitigate contaminant pathways and do what is needed to obtain guideline values once again. Fencing of waterways have been identified as a priority by the Sustainable Dairying Water Accord launched in 2013. As of May 2017, all stock must be excluded from: (1) any permanent flowing rivers more than a metre wide and 30cm deep, (2) all lakes, and (3) any significant wetlands as identified in a Regional Plan or Policy Statement. This strategy effectively manages direct faecal contamination from stock. The task of eliminating direct pathways of faecal contamination to freshwater is an easier task that eliminating diffuse sources of faecal contamination (Collins et al., 2013). The infiltration rate of water into soil affects the transfer of faecal contaminants to freshwater (Collins et al., 2007). Riparian plantings may assist the contamination to freshwater from diffuse runoff, but may also reduce pathogens. Roots and worms can create porous channels for a preferential flow of water to percolate into soil (Collins et al., 2007; Prosser et al., 2016).

This may increase the amount of subsurface flow, potentially increasing the quantity of pathogens entering freshwater bodies. However, some native species, namely *L. scoparium* and *K. robusta*, exhibit antiseptic properties from root exudates, which could mitigate the threat of microbial contamination of soil (Prosser et al., 2016).

2.6. Other nutrients

2.6.1. Sulphur

Sulphur (S) is naturally derived from soil parent materials and atmospheric inputs. It is cycled through the environment from above and below-ground transformations (Figure 2-5). Total soil S can range from 0.01 % to more than 0.1 % of bulk soil (McLaren and Cameron, 1996). Sulphur has many forms in soil, the two primary forms are inorganic and organic S (Metson and Blakemore, 1978). Organic S accounts for some 90% of S in most topsoil. Sulphate (SO_4^{2-}) is the form of S available to plants for uptake from soil. Plants can also adsorb SO_2 emissions from the atmosphere (Eriksen, 1997). Similar to the PO_4^{2-} fixation, where PO_4^{2-} becomes adsorbed and occluded, SO_4^{2-} can become adsorbed to soil surfaces and undergo occlusion (Metson and Blakemore, 1978). Occluded SO_4^{2-} is unavailable for plant uptake. Metson and Blakemore (1978) found that weakly bound SO_4^{2-} was rapidly replaced by PO_4^{2-}, following addition of superphosphate. The SO_4^{2-} ion is extremely soluble and can therefore leach from the soil in high quantities (McLaren and Cameron, 1996). Leaching of SO_4^{2-} can potentially be amplified with the addition of P to soil, as SO_4^{2-} is displaced (Metson and Blakemore, 1978). Sulphate may be lost from soil following reduction to hydrogen sulphide (H_2S).

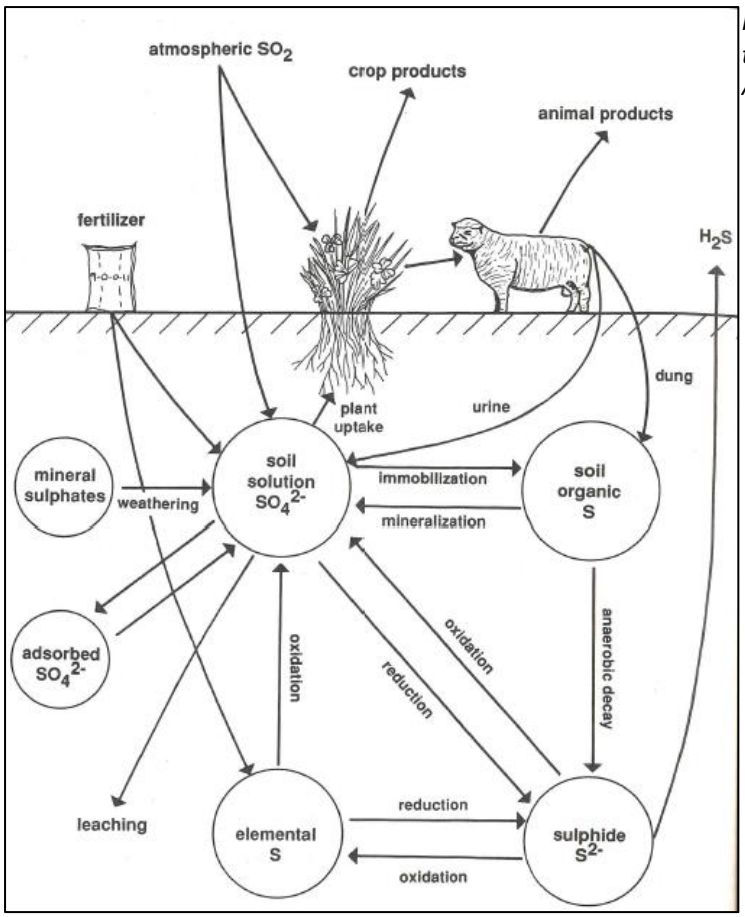


Figure 2-5: Above and below-ground transformations of the Sulphur Cycle. Adapted from McLaren & Cameron 1996

2.6.2. Potassium

Potassium (K) generally accounts for 0.1 – 4% of the total weight in soils (McLaren and Cameron, 1996). Total K has four major forms in the soil, each having different availability properties to plants. (1) Mineral K (90 – 98% of total K) is nearly completely unavailable for plants. Primary minerals, such as feldspars and micas, are extremely important for long-term availability of K in soil. (2) Fixed K (1 – 10% of total K) becomes slowly available to plants when K^+ is released. K^+, like NH_4^+, binds readily to soil colloids, rendering it unavailable to plant uptake. Exchangeable K (1 – 2% of total K) and soil K (0.1 - 0.2% of total K) are in an equilibrium (McLaren and Cameron, 1996).

2.6.3. Calcium

Calcium (Ca) is the fifth most abundant element in the earth's crust. Ca is found predominantly in minerals such as feldspar, apatite (Ca-phosphates) and calcite ($CaCO_3$) (McLaren and Cameron, 1996). The amount of Ca found in soil depends on the dominant parent material and the extent of weathering

processes. However, Ca is also added from lime and superphosphate fertilisers (McLaren and Cameron, 1996).

2.6.4. Magnesium

Magnesium (Mg) roughly composes 2% of the earth's crust. It is found in minerals such as dolomite, biotite and serpentine (McLaren and Cameron, 1996). Magnesium is essential for both plants and animals. Magnesium is found in three forms in soil: i) Mineral Mg, ii) Exchangeable Mg, and iii) soil solution Mg (McLaren and Cameron, 1996). Most Mg is found in mineral Mg and released slowly through weathering processes for more plant available forms.

3. Vegetation and site selection

This chapter describes the native plant species selected for this research, including foliage and root-systems. As this research project was one year from start to finish, native species had to be pre-existing at each sampling site. This reduced the availability of native species for selection. Adequate time had to be taken to scout an area for pre-existing vegetation, to ensure that the correct vegetation was available and easy to access. Permission from landowners was sought before sampling.

3.1. Vegetation Selection

Native plant species used for riparian restoration planting throughout NZ were selected, as preferred to non-native species. Sampling sites were selected upon the availability of suitable NZ-native species. Five native species were selected, along with non-native *Lolium perenne* (Table 3-1). *L. perenne* was found in agricultural land adjacent to the riparian zone at each sampling site. It acts as a control for chemical concentrations in this study. Native vegetation, at each respective site, was compared to *L. perenne* concentrations in the adjacent land.NZ agricultural industries have traditionally relied on *T. repens* for *L. perenne* to flourish. However, due to the increase of fertiliser use, *T. repens* has decreased (van den Pol et al., 2015).

Table 3-1: An overview of the native species sampled, including their common name, Maori name, scientific name and family.

Common Name	**Maori Name**	**Scientific Name**	**Family**
New Zealand Flax	Harakeke	*Phormium tenax (J.R. Forst & G. Forst)*	*Hermerocallidaceae*
Kānuka	Kānuka	*Kunzea robusta (de Lange & Toelken)*	*Myrtaceae*
Mānuka	Kānuka	*Leptospermum scoparium (J.R. Forst & G. Forst)*	*Myrtaceae*
Karamu	Karamu	*Coprosma robusta (Raoul)*	*Rubiaceae*
Lemonwood	Tarata	*Pittosporum eugenioides (A. Cunn)*	*Pittosporceae*
Perennial Ryegrass	N/A	*Lolium perenne (L.)*	*Poaceae*

3.2. Species Description

3.2.1. Phormium tenax, New Zealand Flax, Harakeke

Phormium tenax [J.R. Forst & G. Forst] (*P. tenax*) has historical, ecological, cultural and economic values for NZ. A monocotyledon, endemic to NZ, Norfolk Island, and the Chatham Islands, *P. tenax* is one of only two species of the genus *Phormium* (Wehi and Clarkson, 2007). *P. tenax* is the most popular NZ native species used in restorative riparian planting, along with other NZ-native sedges (Renouf and Harding, 2015). Renouf and Harding (2015) found that *P. tenax*, along with native sedges, are the only native species that were dominant in restorative riparian plantings throughout the Canterbury region. Foliage colours vary from a yellow-green to a dark, deep green (Figure 3-1). The youngest leaves are located in the middle of the plant and sprawl outwards in a fan-like orientation (Critchfield, 1951). The longest leaves can grow to 3 m in length and 120 mm in diameter. Native birds pollinate the red/brown flowers on tall stalks that can grow to 5 m in length. Due to the tough, fibrous leaf structure, Maori have historically used *P. tenax* to weave items such as nets, clothing and baskets (Wehi and Clarkson, 2007).

P. tenax roots extend the same distance vertically and laterally as the above-ground bush. Most roots are in the top 0.5 m of soil, with a radius of roughly 1.5 m (McGruddy, 2006). *P. tenax* are thought as suitable for restoration programs due to roots that penetrate deep and have high water-absorbing potential. However, to thrive in riparian initiatives, *P. tenax* requires a well-drained, organic soil (Wardle, 1991).

3.2.2. Kunzea robusta, Kānuka

Kunzea robusta [de Lange & Toelken] (*K. robusta*) is a member of the *Myrtaceae* family. *K. robusta* is often mistaken for *Leptospermum scoparium* ([J.R. Forst & G. Forst]) (*L. scoparium*), as they have similar physical properties (Essien et al., 2019). The simplest method of distinguishing between the two plants is to touch the foliage. *K. robusta* have softer leaves, while *L. scoparium* leaves are typically sharper to the touch (de Lange, 2014). However, the most reliable method of distinguishing between the two is to identify the capsules. *K. robusta* have smaller (4-5 mm) capsules and *L. scoparium* have larger (8-10 mm) capsules. *K. robusta* trees are found in coastal to low alpine (1600m) landscapes. The leaves are a yellow-green colour and small in size; 4.0-25.0 x 0.5-1.8 mm (Figures 3-2 & 3-3). *K. robusta* flowers are white, and typically have five orbicular petals surrounding an orange-brown circular seed (de Lange, 2014; Essien et al., 2019). *K. robusta* can live for 60 to 150 years, and can grow to heights of 30m with a trunk up to 1m in diameter (de Lange, 2014).

Essential oils can be extracted from the leaves. The yield and content of the essential oils depends on the extraction method, temperature, part of *K. robusta* used and other physicochemical properties (Harris et al., 2004). Essential oils from *K. robusta* have been reported to have anti-inflammatory (Chen et al., 2016), antibacterial & antifungal (Lis-Balchin et al., 2000) properties, at varying levels of success.

K. robusta was not studied by Marden et al. (2007), but it is likely to have a heart-rooted system. Heart-rooted systems originate from or near the root bole in a compact system (Marden et al., 2007). Roots descend vertically or obliquely to vertical lengths of over 2 m (Phillips, 2005). Watson et al. (1999) correlated root depth to the stoniness and depth of loose soil on a given slope, not necessarily the age of the plant. For the first six years of growth, roots will have an average lateral growth of 0.25 m/year (Watson et al., 1999). *K. robusta* requires a well-drained soil to survive in riparian initiatives (Essien et al., 2019).

Figure 3-1: A row Phormium tenax bushes located at Silver Ferns Farms Pareora

Figure 3-3: Close up of K. robusta leaves.

Figure 3-2: K. robusta tree located at Hart's Creek

3.2.3. Leptospermum scoparium, Mānuka

L. scoparium is a member of the *Myrtaceae* family (Essien et al., 2019). *L. scoparium* is smaller than *K. robusta*, usually growing 4-8 m in height (Derraik, 2008), but has been recorded to reach up to 12 m (Ronghua et al., 1984). The leaves are a dark-green, and vary in size from 7-20 mm x 2-6 mm (Stephens et al., 2005) (Figure 3-4). Flowers are most often white, but on rare occasions may be pink or red and are 8-12mm in diameter.

Of all the NZ native species, *L. scoparium* has the greatest economic potential (Reis et al., 2017). Maori traditionally used the plant for medicine, food and timber. Its primary economical use has shifted to essential oils and Mānuka honey (Alvarez-Suarez et al., 2014). The chemical composition of essential oils varies within the *L. scoparium* population. The variety depends on plant age, environmental conditions, geographic location and distillation procedure (Stephens et al., 2005). *L. scoparium* honey has antibacterial properties, exterminating bacteria and inhibiting pathogens within the human body, an appealing attribute of an everyday food-item (Carter et al., 2016).

L. scoparium have a heart-rooted system, a compact system with slanting roots (Figure 3-5). In the first year of growth, roots descend rapidly to 0.2 m, but slow in the next four years to reach 0.25 – 0.3 m (Marden et al., 2007). However, roots rapidly spread laterally in the initial five years, to 1.5 m. *L. scoparium* is adaptable to many soils. It can tolerate low fertility, high acidity and severe exposure to high winds, unlike many other woody species in NZ (Burrows, 1973; Derraik, 2008). Contrary to *K. robusta*, *L. scoparium* can grow in water-logged landscapes and can tolerate continuous flooding for prolonged periods, making it ideal for low-lying wetland restoration projects (Derraik, 2008; Essien et al., 2019).

Figure 3-4: L. scoparium tree located at Hart's Creek. Note the larger capsules on this plant, compared to K. robusta in figures 3-2 & 3-3.

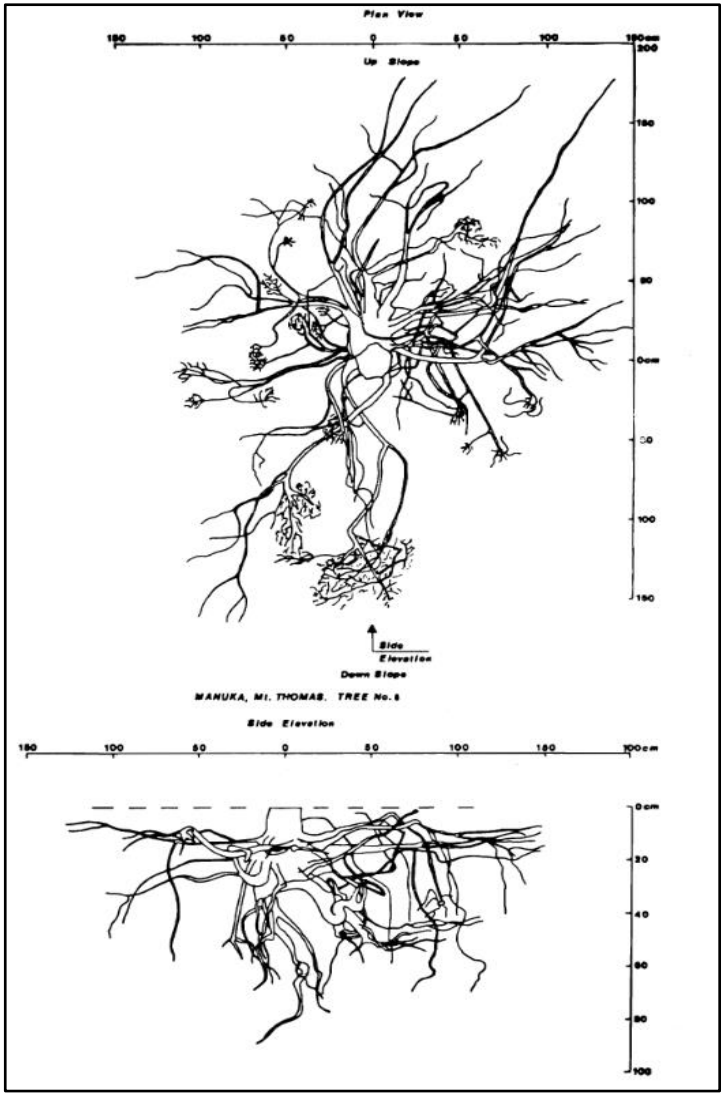


Figure 3-5: A graphic visualisation of L. scoparium roots spreading in soil
Watson and O'Loughlin 1985

3.2.4. Coprosma robusta, Karamu

Coprosma robusta [Raoul] (*C. robusta*) is a member of the *Rubiaceae* family (Stewart, 1993). *C. robusta* is found throughout NZ, from coastal scrubland through to lowland forest (Poole and Adams, 1964). *C. robusta* is a shrub that can grow up to 6m in height. Leaves are a shining green colour and have an elliptic-oblong shape that have a length of 50 – 120 mm and a diameter of 30 – 50 mm (Poole and Adams, 1964; Stewart, 1993) (Figure 3-7). *C. robusta* produces a small, red berry-looking fruit called Drupes, which are eaten by native birds. Flowers are a greenish-yellow colour and accumulate in a dense cluster (Poole and Adams, 1964; Stewart, 1993).

C. robusta has a heart-rooted system, similar to *K. robusta* and *L. scoparium* (Marden et al., 2007). Marden et al. (2007) recorded an average maximum root depth of 0.15 m after one year, growing to 0.35m after five years. Lateral root spread grew from 0.2 m in the first year to 1.5 m after five years.

3.2.5. Pittosporum eugenioides, Lemonwood, Tarata

Pittosporum eugenioides [A. Cunn] (*P. eugenioides*) is a member of the *Pittosporaceae* family (Stewart, 1993). *P. eugenioides* is mostly found in lowland forests scattered throughout NZ. *P. eugenioides* is a small, rounded tree that can grow to a height of 13m, and have a trunk diameter of 0.6 m (Poole and Adams, 1964; Stewart, 1993). Leaves are a glossy, light yellow-green colour (Figure 3-6). They are oblong in shape and their length is 5-10 cm long. Leaves emanate a slight lemon scent when crushed (Poole and Adams, 1964).

P. eugenioides has a heart-rooted system. Marden et al. (2007) recorded an average maximum root depth of 0.2 m after one year, growing to 0.25 m after five years. However, of all the native plant root systems described by Marden et al. (2007), *P. eugenioides* had the greatest mean maximum spread of 3m after five years. The distribution of roots laterally were asymmetric, as large areas of soil were absent of roots. Branching of the roots is a common feature at the extremities.

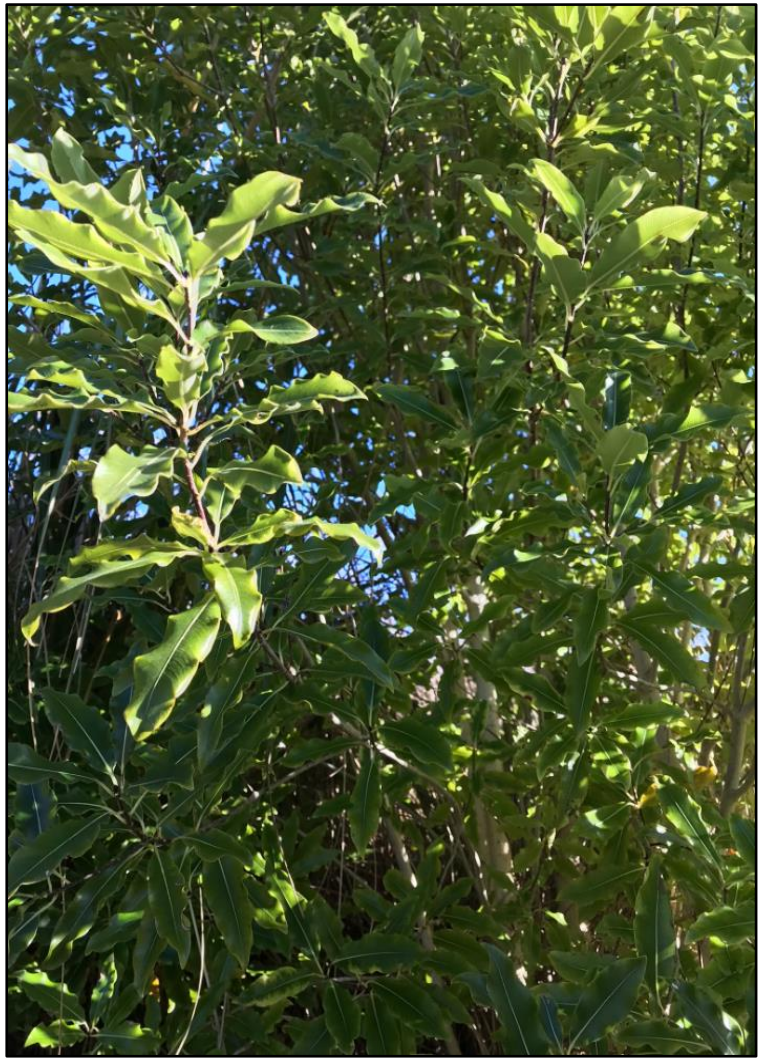


Figure 3-6: P. eugenioides tree located at Birdlings Brook.

Figure 3-7: A small (<2m) C. robusta tree at Lake Waikare.

3.2.6. Lolium perenne, perennial ryegrass

Lolium perenne ([C. Linnaeus]) (*L. perenne*) is the most widely used temperate grass in NZ (Figure 3-8). It is proven to have high yields, easy to establish and grow, can be used in intensive grazing and adapted to fit a wide range of farm management practices (Easton et al., 2011). It is used for long-term pasture systems with fertile conditions. It is compatible with *T. repens* and other pasture species (Charlton and Stewart, 1999). This was significant when it was introduced, as *T. repens* was a primary source of N for many farming practices. *L. perenne* is used in NZ primarily for farming livestock, as it can withstand treading and grazing. However, it requires moist fertile conditions as it performs poorly during hot dry conditions. The root system is shallow, with some 80% of the root mass in the top 0.15 m of soil (Bolinder et al., 2002). Another potential issue for *L. perenne* is the formation of endophyte toxins that may be present within fresh pasture (Charlton and Stewart, 1999). Endophyte toxins are a fungus that pose a risk to livestock and if not dealt with accordingly, can be detrimental (Pirelli et al., 2016). Resowing endophyte-free pasture every 1-5 years (depending on environmental conditions) will assist with keeping endophyte levels down (Charlton and Stewart, 1999).

Figure 3-8: A soil pit dug to sample L. perenne in the adjacent paddock to native vegetation at Lake Waikare.

3.3. Site Selection

Four sampling sites at native riparian restoration sites in Canterbury and Waikato were selected for the field study. Each site had a well-established riparian zone, but varied between age and species. As riparian sites were already established, the native species present at each site was a significant factor in deciding the plant selection. Control samples were collected from adjacent pasture, containing ryegrass. Adjacent pasture at each site had a history of agricultural production.

Three locations were in the South Island, at Silver Ferns Farms Pareora (SFFP), Hart's Creek and Birdlings Brook respectively (Figure 3-9). Although Hart's Creek and Birdlings Brook were two separate sampling sites, they both were on the south face of Lake Ellesmere, had similar species diversity, age and soil types. Therefore, the results have been combined from both sites and are reported as 'Lake Ellesmere Tributaries'. The remaining location was in the North Island, on the south face of Lake Waikare. Each sample site was unique, as they each had a different mix of native plants and different agricultural activity in the adjacent paddock. In total, there were 164 soil samples taken across all sites and vegetation.

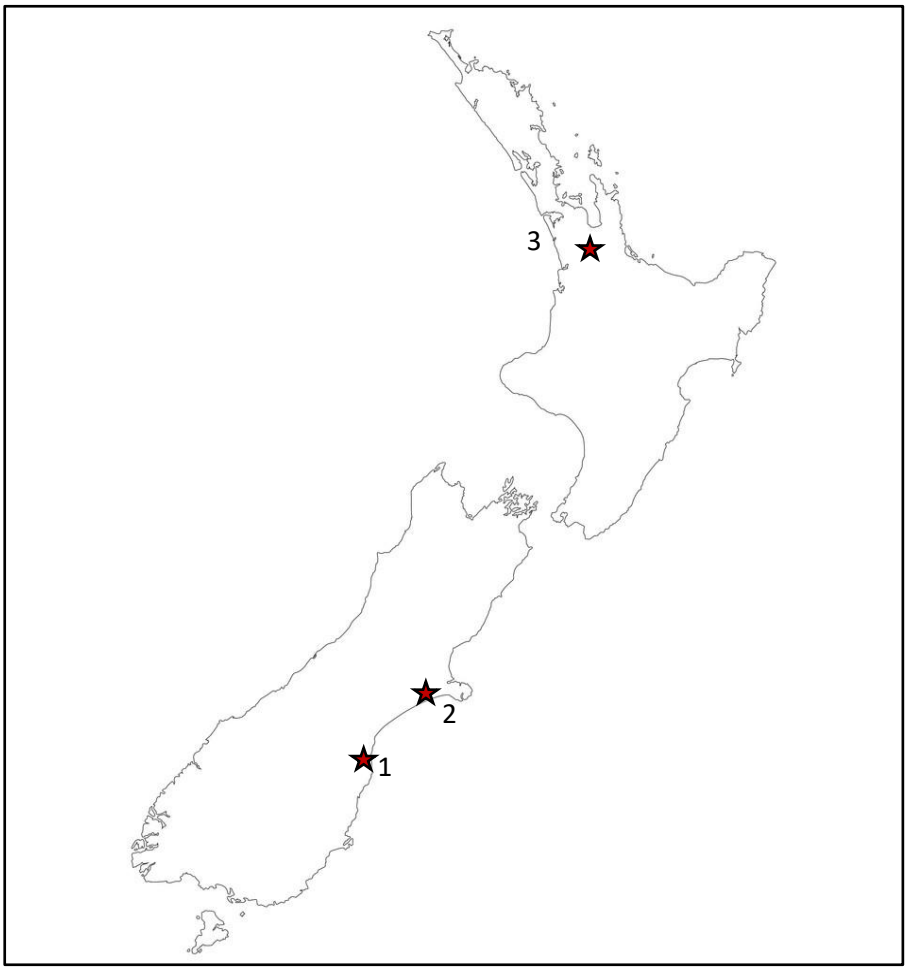


Figure 3-9: The locations of each sampling site within New Zealand.

1 = Pareora

2 = Lake Ellesmere tributaries

3 = Lake Waikare

3.3.1. Silver Ferns Farms Pareora (44°28'50.6"S 171°13'01.8"E)

Permission was granted by Daryn Jemmett (Group Environmental Manager) & Phil McGuigan (Environmental Land Manager) at SFFP to gather soil samples to analyse. Robert Grant (Pareora Farm Manager) was the onsite contact at SFFP. He provided an induction and a tour of the farm. While working onsite, I was accompanied by Lindsay Paul (General Farm-hand), who kindly assisted with soil collection. The farming practices at SFFP where samples were taken was to grow pasture. No stock had access to this pasture.

Wastewater at SFFP generated from meat processing must be appropriately discharged as to not break the conditions of their consent. Historically, SFFP has discharged 100% of their wastewater into the ocean. However, during 2018, 50% of wastewater on average was discharged to land through five fixed centre-pivot irrigators and K-lines (Conway et al., 2018). Under the fixed centre-pivot irrigators, perennial ryegrass is cut-and-carried and sold for feed. SFFP report adding lime and S to these paddocks to reduce sodium (Na) concentrations and avoid mineral accumulation (Conway et al., 2018). Nutrients and chemicals that are susceptible to leaching may follow the natural flow of groundwater to a small stream, dominated by a monoculture of *P. tenax*. The width of the riparian zone was one bush wide (<5m width). This is the only riparian zone at SFFP with native planting. SFFP have plans to construct additional riparian zones at another small stream on site.

The soil at SFFP is a silty loam, fragic pallic derived from schist or greywacke. Fragic pallic soils are dry in the summer while can be saturated in the winter, have weak structure but high density and a low content of iron oxides. The drainage of water through soils are slow and they are susceptible to erosion.

Control samples were collected from the soil containing *L. perenne* under four fixed centre-pivot irrigators, at depths of 0-10 cm, 10-30 cm, 30-45 cm and 45-60 cm (Figure 3-10). Rhizosphere soils from *P. tenax* were collected from five locations along the riparian zone, and at depths of 0-10 cm, 10-30cm, 30-45cm & 45-60 cm (Figure 3-11). Samples were collected between the 14-15/05/19.

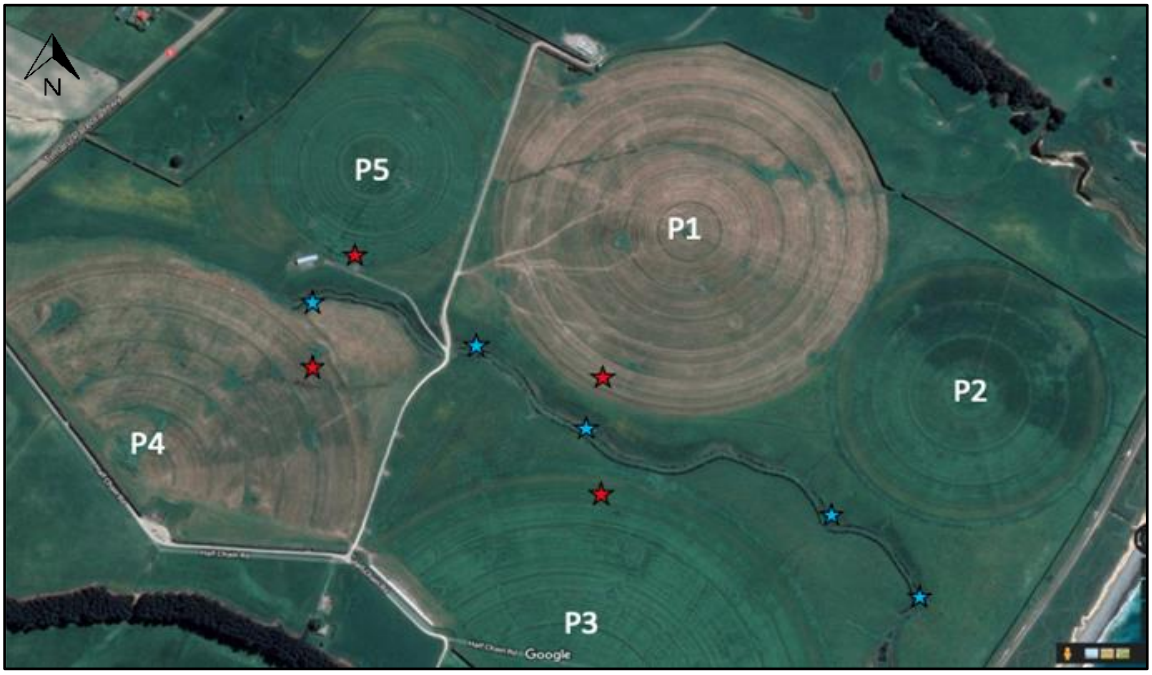


Figure 3-10: A bird's eye view of Pareora, showing the sampling plan that was used. The red stars indicate where soil under L. perenne was sampled. The blue stars indicated where P. tenax was sampled.

Figure 3-11: A 60 cm soil pit that was dug at Pareora to gather soil at each depth beside P. tenax.

3.3.2. Birdlings Brook (43°47'39.5"S 172°18'49.5"E) and Harts Creek (43°48'11.4"S 172°19'03.3"E)

The sampling site at Birdlings Brook was accessed from John Leggs' Farm. This farm is used for dairy cow holding and grazing. However, it has not had fertiliser application for the past two years. Birdlings Brook stream flows into the lower part of Harts Creek, which discharges into Lake Ellesmere. Riparian zones to the south of Lake Ellesmere are experiencing native restoration programmes. Locals have removed mature willows and replaced them with a diverse range of NZ native vegetation. This restoration is still ongoing at many sites. The vegetation at this particular site was relatively new, at about 10 years old. Native vegetation that was selected to be sampled from this location were *P. tenax*, *K. robusta* and *P. eugenioides.*

The soil at Birdlings Brook is a silty loam Orthic Gley that represents the original extent of a NZ wetland. Orthic Gley soils are commonly water logged, have a high bulk density, high organic matter and soil organisms are usually restricted because of anaerobic conditions.

Control samples were collected from the adjacent paddock, at depths of 0-10cm, 10-30cm, 30-45cm and 45-60cm (Figure 3-12). Rhizosphere soils were collected from two *K. robusta*, *P. tenax* and *P. eugenioides* plants, respectively, at depths of 0-10 cm, 10-30 cm, 30-45 cm and 45-60 cm. Samples were collected on the 26/06/19.

Figure 3-12: A bird's eye view of Birdlings Brook. The vegetated cover in the middle is where the sampling for native vegetation took place.

The sampling site at Harts Creek was accessed from the public bridge along Creamery Road (Figure 3-13). Similar to Birdlings Brook, Harts Creek has undergone restoration of diverse NZ-species. The vegetation sampled at this site were 10-15 years old, a similar age to the vegetation at Birdlings Brook. Vegetation selected to sample here were *P. tenax, K. robusta, P. eugenioides, L. scoparium* and *C. robusta.* The adjacent field was used for primary production.

The soil at Harts Creek is a silty loam Orthic Gley that represents the original extent of a NZ wetland (S-map reference), similar to the soil at Birdlings Brook. Water logging is common during winter periods.

Control samples were collected from the adjacent paddock, at depths of 0-10 cm, 10-30 cm, 30-45 cm and 45-60 cm. Rhizosphere soils were collected from two *P. tenax* plants and one *P. eugenioides*, *C. robusta*, *K. robusta* and *L. scoparium* plants, respectively, at depths of 0-15 cm, 15-30cm, 30-45cm, 45-60cm. Samples were collected on the 28/06/19.

Figure 3-13: A bird's eye view of Hart's Creek. Creamery Road runs from SE to NW. Sampling took place to the left hand side of the bridge on Creamery's Road.

3.3.3. Lake Waikare (37°28'26.8"S 175°13'56.3"E)

The sampling site at Lake Waikare was accessed from Tahuna Road. Permission was granted from Tawera Nikau, the farm owner, to collect samples from his land. Tawera donated a small section of his land to plant NZ native vegetation in June and October of 2017. He, and the Matahuru iwi, are passionate about restoring Lake Waikare. They have invited scientists, the Waikato Regional Council and other NGO's to monitor, sample and analyse the effects of reintroducing native plants to this area. Lake Waikare is a Hypereutrophic Lake with high suspended sediment loads restricting light for macrophyte growth and frequently suffers from algal blooms. Lake Waikare was historically a 'food-bowl' for the ancestors of the Matahuru iwi, before the wetlands were drained for farming. The land adjacent to the sampling site has been used for dairy farming for decades. Tawera's vision, shared with the local iwi, is to plant native riparian vegetation around the entire lake edge to protect Lake Waikare from the adjacent land. Tawera reports that plants here are growing at more than one meter per year.

The soil at Lake Waikare is an Orthic Gley soil that represents the original extent of NZ wetlands. The soil shares similar key features to those at Hart's Creek & Birdlings Brook.

Samples were collected from the south side of Lake Waikare, near the Matahuru Marae (Figure 3-14). Control samples were taken from the adjacent paddock, at depths of 0-10cm, 10-30cm and 30-45cm. Maria Gutierrez-Gines and her team from the Institute for Environmental Science Research (ESR) collected rhizosphere soil samples from *L. scoparium* and mixed species, at depths of 0-10cm, 10-30cm and 30-45cm on the 10-11/12/2018. Additional rhizosphere soil samples from Karamu species, at depths of 0-10cm, 10-30cm & 30-45cm were collected on the 2-3/07/2019.

Figure 3-14: A bird's eye view of the Lake Waikare sampling location. The white box indicates the area that has been put aside for riparian planting. Although this image does not show it, this has had vegetation present since 2017. Samples were collected within the boundaries of the white box.

4. Methods

4.1. Soil preparation

4.1.1. Soil drying

Soil samples were dried on an aluminium tray in a large drying oven at 40 °C for 96 hours (Figure 4-1). Apart from KCl extraction and moisture content, every other analytical analysis technique used the oven dried soil samples. A pestle and mortar was used to crush the soil break soil aggregates. The pestle and mortar were washed with deionised water, followed by a rinse of ethanol and dried between each soil sample. This was rigorously maintained to ensure there was no cross-contamination between soil samples. The ground soil was passed through a 2 mm research grade sieve to remove excess vegetation and homogenise the soil. The short abbreviation of "air-dried, <2 mm" in the method section indicates this procedure has been performed on the soil samples.

Figure 4-1: Drying oven used to dry all soil samples.

Following drying and sieving, soils were crushed using a ring mill grinder in the School of Earth and Environment department at the University of Canterbury. Between every run, the ring mill was washed thoroughly with D.I. water and then rinsed with ethanol before being used for the next soil sample. Each sample took, on average ten minutes, to grind soil and wash the ring mill. The result was a dry fine soil which was used for the chemical analysis.

4.1.2. Potassium Chloride extraction

Soils used for the potassium chloride (KCl) extraction were moist and had not undergone the soil drying method as stated in section 4.1.1.

40mL of 2M potassium chloride was added to a 4 g ± 0.05 sample of moist soil and shaken for 1 hour. Samples were centrifuged at 2000 rpm for 10 minutes and filtered through a Whatman No. 41 filter pad (Blakemore, 1987). KCl extracts were frozen, until spectroscopic analysis for NO_3^- and NH_4^+. Spectroscopic methods for NO_3^- and NH_4^+ used this KCl extraction method and are recorded in sections 4.2.3 and 4.2.4 respectively.

4.2. Chemical tests

4.2.1. pH

10 g of soil (air-dried, <2 mm) was weighed and stirred with 25 mL of deionized water. The solution was left to stabilize for 24 hours before being analysed using a HACH HQ440-d-multi pH reader (Blakemore, 1987).

4.2.2. Moisture content

Sub-samples of moist soil (10 – 20 g) were weighed into new cupcake cases and dried at 105 °C for 24 hours. Each cupcake case was weighed individually before weighing in the moist soil. Sub-soils were cooled to room temperature and immediately weighed to three decimal places (Blakemore, 1987). Moisture content was calculated using the equation below (Eq. 4-1).

$$\text{Moisture Content } \% = \frac{(\text{Wet soil weight} - \text{Dry soil weight})}{(\text{Wet soil weight})} \text{ x } 100 \qquad \text{(Eq. 4-1)}$$

4.2.3. Nitrate

A 350 µL aliquot of KCl extract was added to a 1.5 mL semi-micro cuvette, followed 350 µL VCl_3, 150 µL *N*-(1-Napthyl) ethylenediamine dihydrochloride (NEDD) and 150 µL sulphanilamide (SULF). It took 45 minutes to reach optimal colour development. A higher concentration of NO_3^- turned the solution a brighter pink colour (Figure 4-3). A calibration curve was constructed using standard concentrations of 0, 0.5, 1, 2, 3 and 5 mg/L against the absorbance reading to give a linear concentration gradient with an R^2 value of 0.991. The solution absorbance were analysed at 540 nm using a Cary 100-bio UV-visible spectrophotometer and plotted along the calibration curve to attain a NO_3^- concentration (Miranda et al., 2001).

4.2.4. Ammonium

A 650 µL aliquot of KCl extract was added to a 1.5 mL semi-micro cuvette, followed by 50 µL of ethylenediaminetetraacetic acid reagent, 200 µL sodium salicylate-sodium nitroprusside and 100 µL buffered hypochlorite. It took 40 minutes to reach optimal colour development. As the concentration of NH_4^+ increased, the colour of the solution turned from a yellow-green through to a dark blue (Figure 4-4). A calibration curve was constructed using standard concentrations of 0, 0.1, 0.2, 0.5, 1 and 2

mg/L against the absorbance reading to give a linear concentration gradient with an R^2 value of 0.999. The solutions were analysed at 667 nm using a Cary 100-bio UV-visible spectrophotometer and plotted along the calibration curve attain an NH_4^+ concentration (Dorich and Nelson, 1983).

4.2.5. Total N & C

The method used to obtain TN and TC could not be replicated with the equipment at the University of Canterbury. As a result, soil and plant samples were sent to Roger Cresswell at Lincoln University to be analysed with Vario-Max CN Elementar Analyser (Elementar®, Germany)

4.2.6. Olsen P

Soil (air-dried, <2 mm) weighed to 1.0 g was added to 20 mL of 0.5 M $NaHCO_3$. The solutions were shaken on end over end shaker for 30 minutes. Followed by centrifuge at 2000 rpm for 10 minutes and filtered through a Whatman No. 42 filter pad to obtain the $NaHCO_3$ extract with no particulates (Olsen, 1954).

A 10 mL aliquot of the extract was added to 50 mL tube, 1-2 drops of p-nitrophenol indicator was added, followed by 1 mL of 2M H_2SO_4 and left to effervescence for 1 hour. 5 mL of working colour reagent was added and filled to 50mL with deionized water (Blakemore et al. 1987). Optimal colour development took 30 minutes. As concentration of soluble P increased, a deeper blue was observed (Figure 4-2). A calibration curve was constructed using standard concentrations of 0, 0.2, 0.4, 0.8, 1.2, 1.6, 2 and 5 mg/L against the absorbance reading to give a linear concentration gradient with an R^2 value of 0.999. The solutions were analysed at 880nm using a Cary 100-bio UV-visible spectrophotometer and plotted along the calibration curve to attain an Olsen-P concentration (Olsen, 1954).

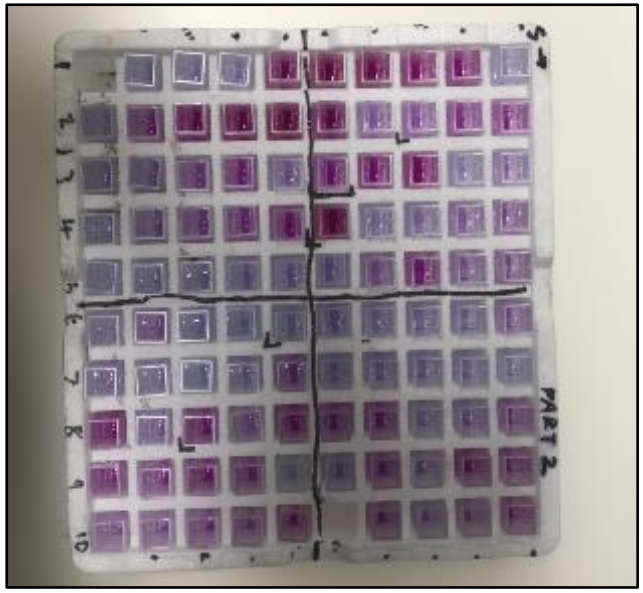


Figure 4-3: Colour formation of KCl extract for analysis of NO_3^-.

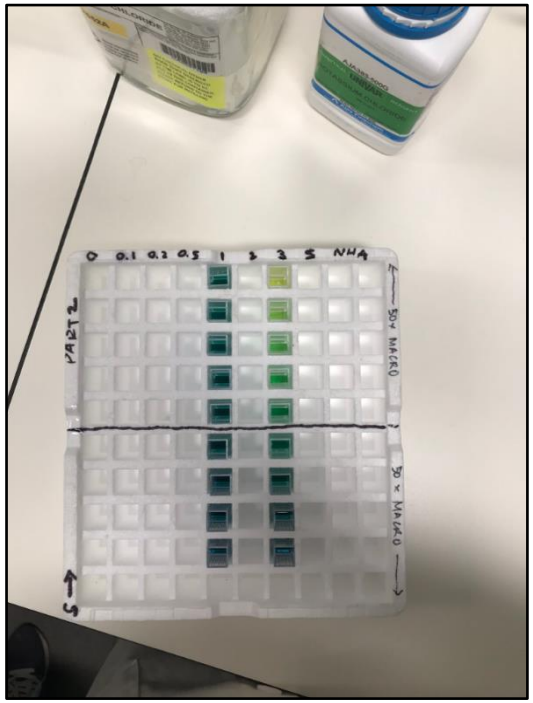


Figure 4-4: Colour formation of KCl extract for analysis of NH_4^+.

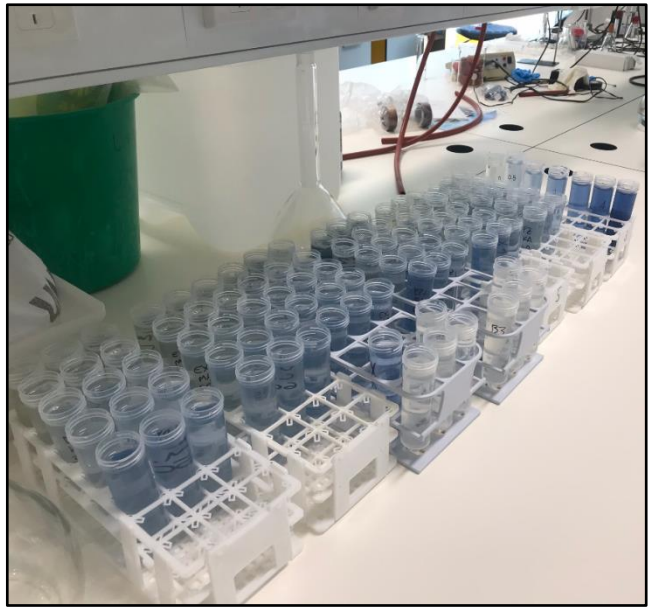


Figure 4-2: Colour formation for analysis of Olsen P

4.2.7. Sulphate

Soil (air-dried, <2mm) weighed to 5.0 g samples were added to 25 mL of 0.01M calcium tetrahydrogen di-orthophosphate. The solution was shaken end over end for 1 hour, then centrifuged at 2000rpm for 15 minutes and filtered through a Whatman No (Blakemore, 1987). 42 filter pad. Extracts were put into 13mm vials and given to Robert Stainthorpe for analysis via Microwave Plasma coupled to Atomic Emission Spectrometer (MP-AES).

4.2.8. Trace elements

Dried sieved (<2 mm) soil (0.5 g ± 0.02) or plant foliage (0.2 g ± 0.02) were weighed into 50ml Erlenmeyer flasks, followed by 10 mL of concentrated analytical grade nitric acid. An orange/brown gas composed of NO_x's was formed. Flasks were placed on a hotplate to boil for 30-45 minutes until NO_x volatilisation ceased. Solutions were cooled and made up to 15 mL with DI water. Solutions were filtered through Whatman No. 41 filter paper and given to Rob Stainthorpe to analyse on MP-AES.

4.3. Data Analysis

Microsoft Excel 2016 was used for general data management and analysis. All graphs recorded were made using Excel's graphing software. Excel was additionally used for correlation statistics between variables (e.g. NO_3^- and pH). A correlation between analysed samples was performed in excel. Using the data analysis tool pack. Correlations were deemed significant if the p-value was greater than the designated p-value, which was dependent on the sample size.

Minitab (version 18) was the statistical software used for all statistical analysis. A one-way ANOVA was performed between a selected chemical (e.g. NO_3^-) and native vegetation (e.g. *P. tenax*) at a certain depth for each location. Variables were considered significant when $p < 0.05$. A Tukey post-hoc test was used to test differences between variables. Standard errors indicating upper and lower limits, represented on the graphs, were calculated (Eq. 4-2). Where n is the number of samples.

$$std.error = std.dev./\sqrt{n} \quad \text{(Eq. 4-2)}$$

5. Results & Discussion

5.1. pH and gravimetric soil moisture

The average soil pH in the rhizosphere of native vegetation and adjacent pasture ranged from 5.2 to 6.6 (Figure 5-1). At SFFP, the soil pH under *L. perenne* was significantly ($p < 0.05$) higher than *P. tenax*. The higher pH under pasture is likely to be from the application of lime at SFFP. Regular application of lime was applied to maintain soil pH above 6.0, improve soil structure and reduce accumulation of Na in soil (Conway et al., 2018). At the Lake Ellesmere tributaries and Lake Waikare, there was no significant difference in soil pH between *L. perenne* and native vegetation. Lake Waikare had higher soil pH levels than at the Lake Ellesmere tributaries. The average gravimetric soil moisture content (GSMC) ranged from 15 % to 34% (Figure 5-2). At the Lake Ellesmere tributaries, GSMC under *P. tenax* was significantly ($p < 0.05$) higher than GSMC under other native vegetation and *L. perenne*. *P. tenax* at the Lake Ellesmere tributaries was planted closer to the streamside, relative to other native vegetation, which likely would have increased the GSMC. *P. tenax* was two-fold higher at the Lake Ellesmere tributaries than *P. tenax* at SFFP. This difference is likely to be from the difference in soil type. The Lake Ellesmere tributaries has a silty loam orthic gley soil, which frequently become waterlogged. SFFP has a fragic pallic soil, which is dry in summer and often saturated in the winter.

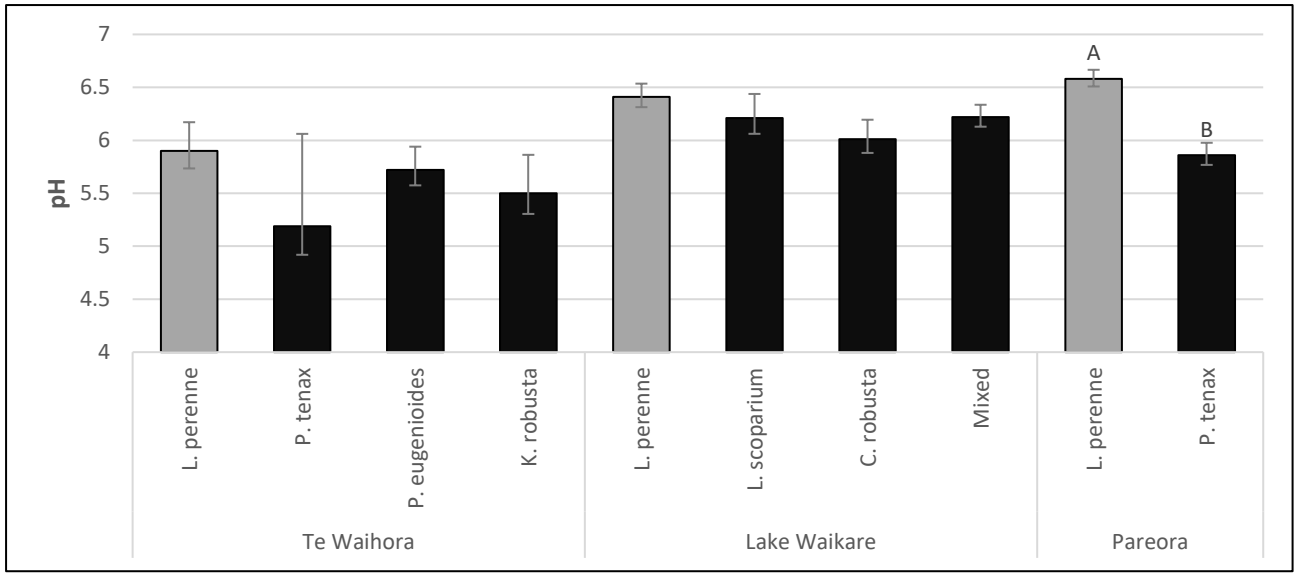


Figure 5-1: Soil pH in the top 150 mm of soil under native vegetation and L. perenne. Native vegetation are in black and non-native are in grey.
Note: "Te Waihora" represents the Lake Ellesmere tributaries

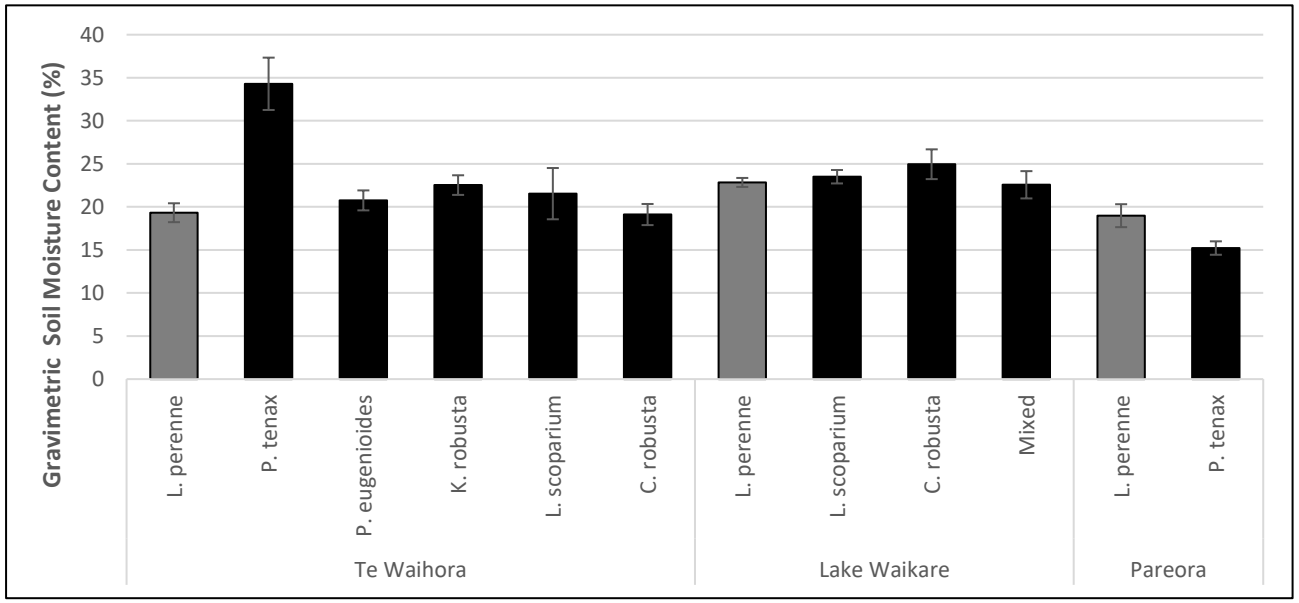


Figure 5-2: The average gravimetric soil moisture content under native vegetation and L. perenne. Native vegetation is in black and non-native are in grey.
Note: "Te Waihora" represents the Lake Ellesmere tributaries.

5.2. Nitrate, Ammonium & Total N

There were no significant differences in TN concentration in the top 0 to 30 cm rhizosphere soil of native species at any sampling sites (Tables 5-1 & 5-2). Similarly, there were no significant differences in TN between *L. perenne* and native vegetation. TN concentration decreased with increased depth. Organic N makes up 94 – 98 % of TN and does not leach, unless converted to NO_3^- (McLaren and Cameron, 1996). TN had significant ($p < 0.05$) positive and negative correlations with pH between 0 to 30 cm at both the Lake Ellesmere tributaries and Lake Waikare (Figures 5-3 & 5-4). At the Lake Ellesmere tributaries, TN and pH were negatively correlated. In contrast, at Lake Waikare TN and pH were positively correlated. Soil acidity and pH have been demonstrated to affect both TN and TC concentrations (Marinos and Bernhardt, 2018). Soil acidity and drainage are important for organic matter decomposition (McLaren and Cameron, 1996). Acidic soils and water-logging both cause a reduction in decomposition. Other physicochemical factors in soil, such as pH, water composition, temperature, C content and nutrient cycling may be why these correlations are different. However, anthropogenic influence from different fertilisation schemes and lime treatment may also affect the correlation (Conway et al., 2018). The roots of *L. scoparium* and *K. robusta* are mostly concentrated in the top 30 cm of soil (Watson and O'Loughlin, 1985). The data in tables 5-1 & 5-2 represent the chemical parameters recorded in the top 0-15 cm and 15-30 cm of soil, respectively. See appendix 1 for the tables with the data for chemicals at 30-45 cm and 45-60 cm.

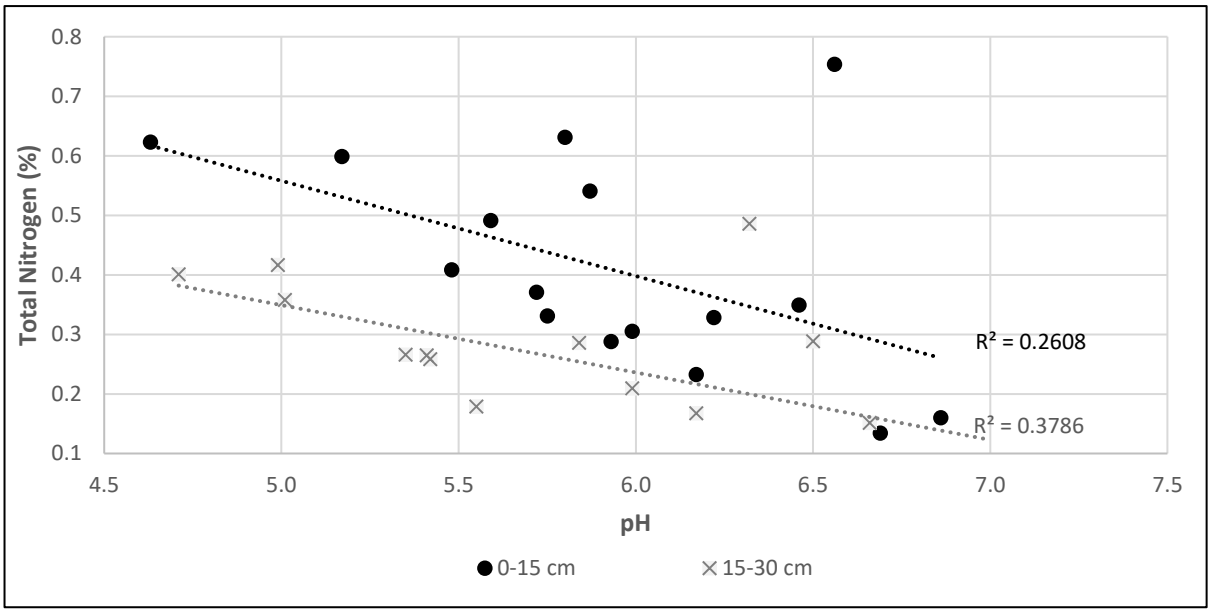


Figure 5-3: Total Nitrogen against pH correlation between 0 to 300 mm of soil at the Lake Ellesmere tributaries.

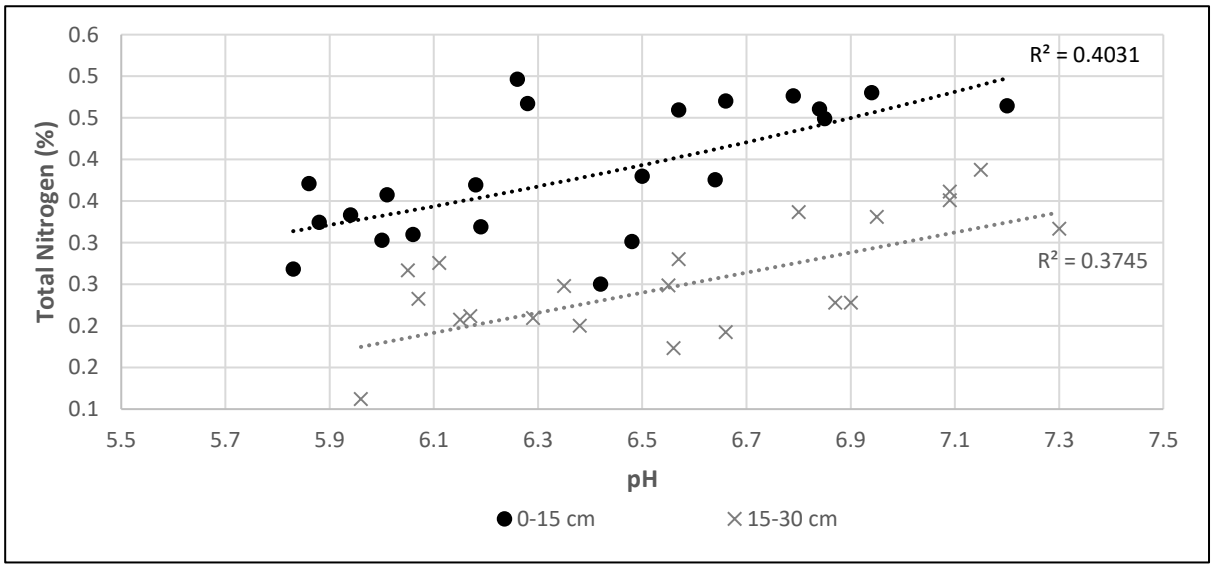


Figure 5-4: Total Nitrogen against pH correlation between 0 - 300 mm of soil in Lake Waikare.

Table 5-1: Means (and standard error ranges) of the chemical parameters analysed in the top 15 cm of soil at each sampling location. The units for all data are mg/kg unless otherwise stated in brackets. Different letters indicate significant differences of that parameter ($p < 0.05$) between species in the same location.
**Geometric mean calculated with the standard error range*

0-15cm	**SFFP**		**Lake Waikare**				**Lake Ellesmere tributaries**			
Chemical	*L. perenne*	*P. tenax*	*L. perenne*	*L. scoparium*	*C. robusta*	*Mixed (L. scoparium)*	*L. perenne*	*P. tenax*	P. eugenioides	K. robusta
pH*	6.6 (6.5 - 6.7) [a]	5.9 (5.8 - 6.0) [b]	6.4 (6.3 - 6.4)	6.2 (6.1 - 6.4)	6.0 (5.9 - 6.2)	6.2 (6.1 - 6.3)	5.9 (5.7 - 6.2)	5.2 (4.9 - 6.1)	5.7 (5.7 - 5.7)	5.5 (5.3 - 5.9)
NO_3^-	11.7 ± 2.1	11.5 ± 3.0	17.9 ± 5.6	14.3 ± 4.5	6.6 ± 1.3	17.5 ± 3.1	4.6 ± 2.0	6.7 ± 3.7	2.5 ± 1.1	15.1 ± 13.3
NH_4^+	4.7 ± 2.3	4.4 ± 0.8	1.9 ± 0.7	2.4 ± 1.2	3.7 ± 0.6	6.4 ± 3.5	10.5 ± 2.5	12.7 ± 4.6	6.9 ± 1.1	10.0 ± 3.5
Total N (%)	0.30 ± .02	0.27 ± .02	0.40 ± .04	0.40 ± 0.03	0.30 ± 0.02	0.39 ± 0.03	0.34 ± 0.07	0.56 ± 0.09	0.32 ± 0.05	0.51 ± 0.11
Total C (%)	3.31 ± 0.23	2.71 ± 0.14	4.33 ± 0.38	4.60 ± 0.41	3.18 ± 0.16	4.16 ± 0.25	3.53 ± 0.76	6.63 ± 1.27	3.69 ± 0.61	5.58 ± 1.24
Olsen P	23. ± 7	11.6 ± 2.0	42 ± 9	52 ± 5	39 ± 4	51 ± 5	12.3 ± 4.2	46 ± 21	21 ± 9	51 ± 22
Total P	63 ± 8 [b]	113 ± 11 [a]	519 ± 129	721 ± 71	710 ± 66	619 ± 39	584 ± 51	715 ± 93	596 ± 31	695 ± 98
Sulphate	23 ± 10	8.8 ± 0.6	7.1 ± 1.2	6.5 ± 1.5	5.3 ± 0.6	7.7 ± 1.7	7.4 ± 2.3 [bc]	50 ± 5 [a]	7.8 ± 0.5 [bc]	15.6 ± 5.7 [b]
Total S	214 ± 50 [b]	438 ± 63 [a]	458 ± 51 [a]	314 ± 38 [b]	285 ± 62 [b]	329 ± 31 [b]	246 ± 68	489 ± 95	231 ± 42	384 ± 104
Total K	1220 ± 170	1400 ± 90	656 ± 66 [bc]	870 ± 65 [a]	601 ± 67 [c]	739 ± 51 [ab]	2240 ± 190	2170 ± 140	2640 ± 200	2350 ± 220
Cu	3.6 ± 0.7	2.4 ± 0.4	7.2 ± 1.0	7.4 ± 1.2	9.2 ± 3.1	8.1 ± 1.3	6.7 ± 0.9	9.3 ± 1.6	7.2 ± 1.2	9.9 ± 0.8
Fe	7720 ± 660 [b]	9270 ± 120 [a]	17560 ± 1980	15920 ± 930	14480 ± 1310	15540 ± 1420	19200 ± 630	19170 ± 1340	21640 ± 2120	19850 ± 2280
Mg	2370 ± 740	1930 ± 750	7950 ± 820	8140 ± 450	7330 ± 610	8140 ± 760	12580 ± 350	12600 ± 710	14350 ± 1200	13000 ± 1270
Mn	276 ± 64 [b]	443 ± 33 [a]	830 ± 186	673 ± 153	566 ± 118	870 ± 155	435 ± 19	427 ± 24	466 ± 58	438 ± 48
Zn	7.3 ± 2.2	4.6 ± 0.5	17.4 ± 3.7	17.5 ± 3.8	22.6 ± 2.0	27.1 ± 1.1	12.8 ± 3.4	24.9 ± 9.2	10.4 ± 5.2	43.4 ± 11.1
Na	325 ± 9 [a]	245 ± 18 [b]	176 ± 23	233 ± 31	209 ± 33	211 ± 12	191 ± 7 [c]	460 ± 36 [a]	265 ± 27 [b]	298 ± 53 [b]
Ca	3820 ± 160	3270 ± 1603	7200 ± 2630	13750 ± 6780	4540 ± 380	4680 ± 640	5880 ± 280	7050 ± 960	6270 ± 590	6250 ± 280

Table 5-2: Means (and standard error ranges) of the chemical parameters analysed between 15 - 30 cm of soil at each sampling location. The units for are mg/kg unless otherwise stated in brackets. Different letters indicate significant differences of that parameter ($p < 0.05$) between species in the same location.
**Geometric mean calculated with standard error range*

15-30cm	**SFFP**		**Lake Waikare**				**Lake Ellesmere tributaries**			
Chemical	*L. perenne*	*P. tenax*	*L. perenne*	*L. scoparium*	*C. robusta*	*Mixed (L. scoparium)*	*L. perenne*	*P. tenax*	P. eugenioides	K. robusta
pH*	6.4 (6.3 - 6.6)	6.1 (5.9 - 6.3)	6.7 (6.6 - 6.8)	6.4 (6.3 - 6.6)	6.2 (6.0 - 6.4)	6.3 (6.2 - 6.4)	5.7 (5.6 - 6.0)	5.3	5.7 (5.5 - 6.1)	5.1 (5.0 - 5.2)
NO_3^-	3.0 ± 1.1	2.6 ± 0.8	3.5 ± 1.4	6.1 ± 2.0	2.6 ± 0.9	5.9 ± 1.1	2.2 ± 1.3	3.1 ± 2.1	2.4 ± 0.6	2.9 ± 2.2
NH_4^+	2.6 ± 1.0	4.1 ± 1.2	3.5 ± 0.7	5.1 ± 1.0	3.3 ± 0.1	6.0 ± 0.8	2.7 ± 0.5	7.9 ± 4.4	6.6 ± 0.7	4.1 ± 1.2
Total N (%)	0.14 ± 0.03	0.15 ± 0.03	0.25 ± 0.04	0.27 ± 0.03	0.19 ± 0.05	0.26 ± 0.02	0.16 ± 0.05	0.37 ± 0.05	0.28 ± 0.04	0.34 ± 0.05
Total C (%)	1.47 ± 0.34	1.54 ± 0.26	2.72 ± 0.40	3.18 ± 0.51	2.11 ± 0.41	2.87 ± 0.21	1.61 ± 0.48	4.91 ± 1.05	3.04 ± 0.37	4.09
Olsen P	18 ± 7	4.5 ± 1.4	18.8 ± 4.8	24.4 ± 5.0	15.1 ± 4.7	24.6 ± 4.1	5.7 ± 3.2	28.2 ± 18.8	15.9 ± 7.3	40.4 ± 15.1
Total P	57 ± 10 ^{b}	112 ± 16 ^{a}	435 ± 103	523 ± 77	408 ± 71	513 ± 35	585 ± 37	637 ± 83	561 ± 28	652 ± 53
Sulphate	25.0 ± 6.1 ^{a}	8.3 ± 2.7 ^{b}	4.1 ± 1.7	5.5 ± 1.5	5.7 ± 1.5	5.4 ± 2.5	5.9 ± 1.9 ^{b}	42.7 ± 20.3 ^{a}	8.3 ± 3.6 ^{b}	58 ± 22 ^{a}
Total S	153 ± 33 ^{b}	414 ± 76 ^{a}	448 ± 69 ^{a}	198 ± 34 ^{b}	245 ± 115 ^{b}	220 ± 27 ^{b}	120 ± 41 ^{c}	373 ± 58 ^{a}	193 ± 49 ^{abc}	320 ± 69 ^{ab}
Total K	1500 ± 240	1140 ± 37	610 ± 57	645 ± 60	482 ± 24	533 ± 22	2330 ± 140	2270 ± 240	2380 ± 66	2400 ± 240
Cu	4.1 ± 1.7	2.2 ± 0.5	6.1 ± 0.7	5.7 ± 1.1	9.2 ± 3.5	5.9 ± 1.4	4.1 ± 0.9	7.7 ± 1.4	6.7 ± 0.4	8.7 ± 1.9
Fe	10440 ± 910	9550 ± 630	18350 ± 1620	17750 ± 1500	12780 ± 1450	15270 ± 1740	23950 ± 2560	22080 ± 1040	21380 ± 830	21710 ± 560
Mg	2900 ± 910	1875 ± 860	8210 ± 620	9030 ± 750	6120 ± 760	8020 ± 940	15630 ± 1540	14430 ± 630	14200 ± 580	14260 ± 270
Mn	393 ± 107	385 ± 32	752 ± 211	542 ± 133	407 ± 162	756 ± 162	488 ± 9	477 ± 82	479 ± 66	445 ± 83
Zn	6.7 ± 2.5	4.3 ± 0.9	15.7 ± 3.5 ^{a}	10.3 ± 1.9 ^{b}	14.2 ± 1.6 ^{ab}	18.8 ± 1.0 ^{a}	7.9 ± 1.8 ^{b}	11.1 ± 4.5 ^{b}	7.3 ± 1.0 ^{b}	32.5 ± 2.3 ^{a}
Na	354 ± 19 ^{a}	243 ± 15 ^{b}	149 ± 12	169 ± 29	166 ± 18	153 ± 9	228 ± 37 ^{c}	427 ± 12 ^{a}	224 ± 16 ^{bc}	346 ± 29 ^{ab}
Ca	3520 ± 260	3020 ± 210	6270 ± 2380	13420 ± 6820	2820 ± 150	4540 ± 1010	6500 ± 750	7300 ± 820	6100 ± 540	6210 ± 180

There were no significant differences in NO_3^- concentrations between rhizosphere soils of native species at any of the sampling sites. Similarly, there were no significant differences in the rhizosphere soil concentration of *L. perenne* when compared to native vegetation. The results showed that soil depth was more important in determining NO_3^- concentration than native species or location. Different soil types at each location will influence NO_3^- in soil, but not as significantly as the soil depth. In most cases, NO_3^- decreased with soil depth. Olarewaju et al. (2009) found the same trend of decreasing NO_3^- concentration with increasing soil depth. The bulk of NO_3^- was concentrated in the topsoil (0-15 cm) and decreased with increased soil depth. This is likely to follow the same trend of TN with soil depth. Nitrification occurs at a maximum rate when soil moisture tension is at -10 kPa (McLaren and Cameron, 1996). This is when water will not percolate downwards naturally from gravity as water is held by soil particles. At this water tension, there is sufficient oxygen in soil pores to enable nitrification. When soil water tension is >0 kPa, water will naturally percolate due to gravity, as the tension exceeds the capacity for soil to hold water. Although soil moisture tension was not recorded in this experiment, this is a significant factor for the transport of NO_3^-. Two other important factors for NO_3^- transport mechanisms are convection and concentration gradients. Nitrate was significantly ($p < 0.05$) and positively correlated with pH in the top 15 cm of soil at Lake Waikare (Figure 5-5). In Figure 5-5 from pH 6 to 7, there was an estimated NO_3^- increase of 20 mg kg^{-1} (Eq. 5-1).

$$y = 0.0015e^{1.3966x} \quad \text{(Eq. 5-1)}$$

Ying et al. (2017) and Kyveryga et al. (2004) found significant positive correlations of nitrification with an increase of soil pH. Higher nitrification rates will encourage more production of NO_3^-. This does not imply an increased concentration of NO_3^-, as this also depends on the rates of NO_3^- losses via leaching, denitrification and plant uptake (McLaren and Cameron, 1996). Figure 5-5 shows an increase of NO_3^- with pH, which indicates a higher rate of nitrification relative to losses of NO_3^- with increasing pH. This indicates that pH is a key factor for nitrification and NO_3^- losses. Sahrawat (2008) records that maximum nitrification rates occur at pH 8.5. As the pH of soil raises closer to 8.5, the rate of nitrification may be increasing faster than NO_3^- is being lost. This result would be an overall increase of NO_3^- with increasing pH.

Contrary to the trend at Lake Waikare, NO_3^- concentration was significantly ($p < 0.05$) and negatively correlated with pH from 0 cm to 30 cm in soil at the Lake Ellesmere tributaries (Figures 5-7 & 5-8). There was a reduction of NO_3^- with an increase of pH. Watros et al. 2018 found both positive and

negative correlations between mineral N and pH at different times of the year. A positive correlation with pH was more common during their study. Olarewaju et al. (2009) found a 14% decrease of NO_3^- in wet seasons compared to dry seasons, showing that a seasonal variation of NO_3^- is possible. This suggests that the time of the year may have influenced the negative correlation recorded at the Lake Ellesmere tributaries. My samples were collected from the Lake Ellesmere tributaries over two days in late June 2019, so an observation between seasons was not possible. A reduction of NO_3^- concentration at higher pH may have been due to higher NO_3^- losses than nitrification. There are other physicochemical factors that could influence the negative correlation of NO_3^- and pH in Figures 5-7 & 5-8. The Lake Ellesmere tributaries and Lake Waikare have loamy Orthic Gley soils. Maag and Vinther (1996) report denitrification rates in loamy soil respond significantly to changes in soil moisture content and temperature. A high soil moisture content (SMC) will increase both NO_3^- leaching and denitrification rates. A higher SMC will generate more water-filled pore space, increasing soil moisture tension which increases percolation of water through soil. The result is higher rates of NO_3^- leaching (Machefert and Dise, 2004). Additionally, SMC can affect biological denitrification (Friedl et al., 2016; Maag and Vinther, 1996). The net chemical reaction for denitrification in soil is:

$$\mathrm{NO_3^- \leftrightarrow NO_2^- \rightarrow NO\ (gas) \rightarrow\ N_2O\ (gas) \rightarrow N_2\ (gas)} \qquad \text{(Eq. 5-2)}$$

Klemedtsson et al. (1988) found that denitrification was at its highest when water-holding capacity (WHC) was at 100%. Maag and Vinther (1996) found that denitrification rates doubled from 40% WHC to 100% WHC, respectively. If soil has anaerobic conditions through high SMC, biological denitrification will use NO_3^- as the electron acceptor as opposed to oxygen and will form gaseous N (McLaren and Cameron, 1996) (Eq. 5-3).

$$\mathrm{C_6H_{12}O_6 + 4NO_3^- \rightarrow 6CO_2 + 6H_2O + 2N_2} \qquad \text{(Eq. 5-3)}$$

Friedl et al. (2016) found that N_2 emissions exceeded N_2O emissions by a factor of 8 and 17 at 80% and 100% WHC, respectively. This shows that N_2 production will be dominant at higher WHC. Loamy Orthic Gley soils are susceptible to water-logging. The soil at the Lake Ellesmere tributaries may have been experiencing higher water-logging at the time of sampling, therefore could potentially have higher anaerobic conditions. The soil at the Lake Ellesmere tributaries had a higher gravimetric soil moisture

content compared to Lake Waikare in the top 30cm at 25.4% compared to 24.5%. This small difference in gravimetric soil moisture content may have contributed to increased leaching and denitrification rates. The optimal temperature for nitrifying bacteria is 25 °C to 35 °C (Haynes, 1986; McLaren and Cameron, 1996). Below 5 °C, nitrification is considered to be at a minimum (McLaren and Cameron, 1996). Maag and Vinther (1996) found that denitrification decreased three-fold from 5 °C to 20 °C respectively. The average high and low temperature at the Lake Ellesmere tributaries the week before sampling was 12 °C and -3 °C, respectively. The average high and low temperature at Lake Waikare the week before sampling was 15 °C and 6 °C. Therefore the lower temperature at the Lake Ellesmere tributaries has both decreased nitrification and increased denitrification. The net result is a less concentration of NO_3^-. Both SMC and temperature are likely to have had an impact on NO_3^- concentration, which may be responsible for the negative correlation with pH.

There were no significant differences in NH_4^+ concentrations between native vegetation. The only significant difference ($p < 0.05$) recorded was a lower concentration in 30-45 cm rhizosphere soil of *C. robusta* at Lake Waikare. Marden et al. (2007) recorded the average root depth of a three- year-old *C. robusta* to be 24 cm. The vegetation at Lake Waikare was two years old at the time of sampling. *C. robusta* roots and would have therefore not had the time required to grow to 30-45 cm depth. The significant difference observed in NH_4^+ concentration cannot be from *C. robusta* roots influencing soil chemistry. The depth of soil was the most important factor for NH_4^+ concentration. There was a significant decrease in NH_4^+ concentration with depth. Ammonium was significantly and negatively correlated with pH in the top 15 cm of soil at Lake Waikare (Figure 5-6) In figure 5-6, from pH 6 to 7, there was a reduction of NH_4^+ concentration of approximately 5 mg kg^{-1} (Eq. 5-4).

$$y = 4E + 12e^{-4.578x} \quad \text{(Eq. 5-4)}$$

There are more cation exchange sites at higher soil pH, as there is more dissociation of functional groups on both organic matter and clay minerals (McLaren and Cameron, 1996). With more clay minerals, there is increased fixation of NH_4^+. Ammonium concentration will therefore decrease as fixation to clay minerals increases. This may explain the observation of a lower NH_4^+ concentration with an increase of pH at Lake Waikare. The higher abundance of clay minerals will have a negligible influence on NO_3^- concentration. Nitrate molecules are repelled from cation exchange sites, due to its negative charge. Therefore, they remain unbound and percolate through the soil profile with soil moisture (McLaren and Cameron, 1996).

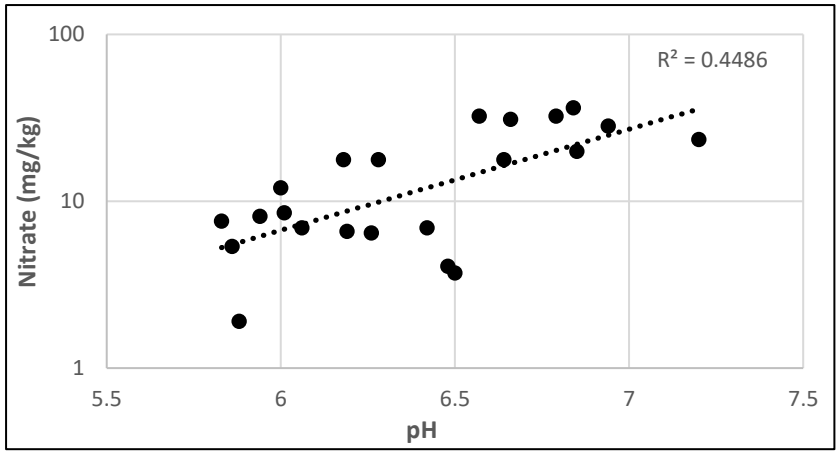


Figure 5-5: Nitrate concentration (mg/kg) against soil pH in the top 150mm of soil at Lake Waikare.

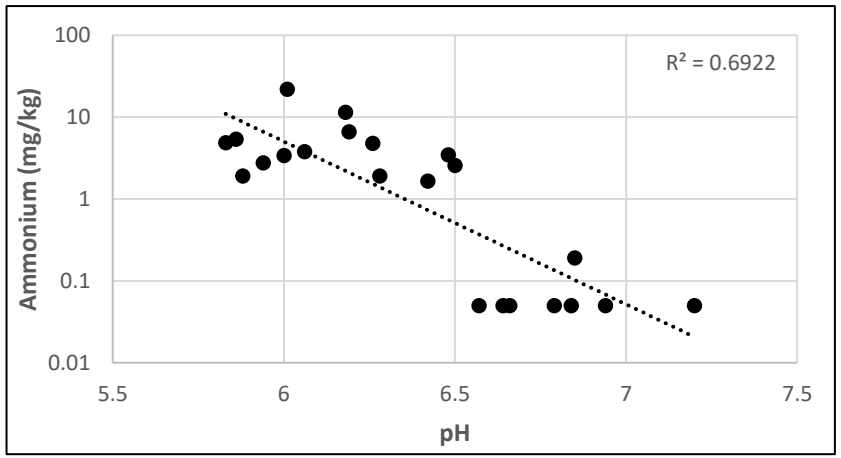


Figure 5-6: Ammonium concentration (mg/kg) against soil pH in the top 150mm of soil at Lake Waikare.

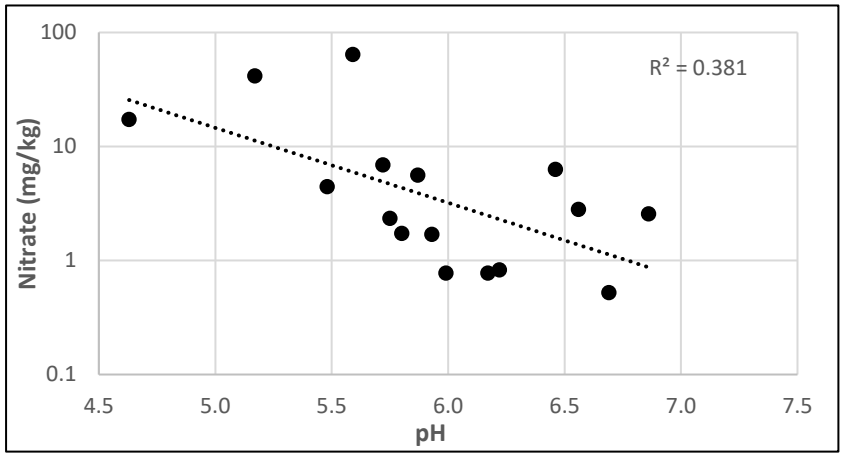


Figure 5-8: Nitrate concentration (mg/kg) against soil pH in the top 150 mm of soil at the Lake Ellesmere tributaries.

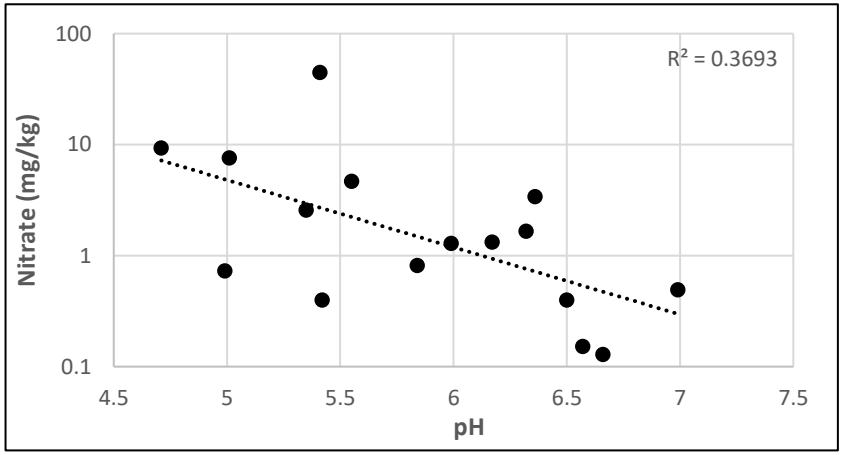


Figure 5-7: Nitrate concentration (mg/kg) against pH between 150 mm and 300 mm soil at the Lake Ellesmere tributaries.

5.3. Total Carbon

There were no significant differences in TC in rhizosphere soil between native vegetation at any of the sampling sites. Total carbon ranged from 1.5 to 6.6% in the top 30 cm of soil across all sampling sites. The results found that TC was significantly and positively correlated with TN at all soils depths and sampling sites. Total carbon decreased with depth. This is expected, as C is added via litter decomposition and sequestering atmospheric CO_2. At SFFP and the Lake Ellesmere tributaries, the C:N ratio decreased with depth (Table 5-3). This observation indicates that more TN relative to TC is entering deeper soils. This suggests that vegetation roots may have an influence on the distribution of TC and TN. Roots create preferential pathways for water flow to percolate through soil (Rao and Puttanna, 2000). Soluble N, in the form of NO_3^-, can infiltrate through preferential pathways to deeper soil. At the well-established riparian zones of SFFP and the Lake Ellesmere tributaries, NO_3^- can follow preferential root pathways. Whereas, at Lake Waikare, the younger roots may not have had sufficient time to establish significant preferential pathways for NO_3^-.

Table 5-3: The C:N ratio of native species, at soils depths of 0-15 cm, 15-30 cm, 30-45 cm & 45-60 cm at SFFP, Lake Waikare & the Lake Ellesmere tributaries.

C:N	**SFFP**		**Lake Waikare**				**Lake Ellesmere tributaries**			
	L. perenne	*P.tenax*	*L. perenne*	*L. scoparium*	*C. robusta*	*Mixed*	*L. perenne*	*P. tenax*	*P. eugenioides*	*K. robusta*
0-15 cm	11.2 ± 0.5^{a}	10.2 ± 0.2^{b}	10.7 ± 0.1	11.4 ± 0.4	10.6 ± 0.3	10.7 ± 0.1	10.5 ± 0.5^{b}	11.9 ± 0.6^{a}	11.4 ± 0.1^{a}	11 ± 0.2^{ab}
15-30 cm	10.4 ± 0.6	9.9 ± 0.3	11.4 ± 0.5	11.6 ± 0.4	11.2 ± 0.7	11.2 ± 0.2	9.4 ± 0.7^{c}	13.1 ± 1.3^{a}	11 ± 0.4^{b}	11.9 ± 0.3^{b}
30-45 cm	8.2 ± 0.4	8.8 ± 1.7	11.4 ± 0.6	11.6 ± 0.6	11.9 ± 0.5	11.5 ± 0.2	8.3 ± 0.8^{c}	12.6 ± 1.1^{a}	10.1 ± 0.6^{b}	11.3 ± 0.2^{a}
45-60 cm	7.7 ± 0.7	7.8 ± 1.2					7.6 ± 0.7^{b}	10.6 ± 1.6^{a}	9.1 ± 0.6^{a}	10 ± 0.3^{a}

5.4. Total P & Olsen P

There were significant differences ($p < 0.05$) in total P (TP) of rhizosphere soil at SFFP. At soil depths 0-15 cm, 15-30 cm & 45-60 cm, *P. tenax* was significantly higher than *L. perenne* (Figure 5-9). Total P recorded at SFFP seemed to be 10 to 20 fold lower than literature values recorded by Burkitt et al. (2009) (1800 mg/kg), Aye et al. (2006) (450-3200 mg/kg) and McLaren and Cameron (1996) (200-1500 mg/kg). All of the samples used the same method to measure TP. However, the concentrations of TP in this study were extraordinarily low. Nonetheless, there may be an explanation as to why the concentration of TP was still higher under *P. tenax* and *L. perenne*. SFFP are replenishing P via wastewater application at an average rate of 70 kg P/ha/year (Conway et al., 2018). However, TP may be removed through *L. perenne* uptake at faster rates than applied, causing a depletion in TP. There was no natural cycling of P due to the cut and carry practices of *L. perenne* at SFFP. Native species did not significantly affect the concentration of Olsen P in rhizosphere soil at any of the sites. Tang et al. (2016) found that Olsen P concentration in the rhizosphere between Durum Wheat and Faba Beans did not vary when exposed to differing levels of P fertilisation. Although not native plants to NZ, this study also found no significant influence by plant roots on Olsen P concentrations in rhizosphere soil. Assuming an average soil density of 1.3 g/cm^3, Olsen P values recorded by SFFP ranged from 15 mg kg^{-1} to 28 mg kg^{-1} (Conway et al., 2018). The values recorded from my study at SFFP in soil from 0 cm to 30 cm ranged from 2 mg kg^{-1} to 42 mg kg^{-1}. Total P and Olsen P had a significant negative correlation with pH in the top 30 cm of soil at the Lake Ellesmere tributaries (Figures 5-10 & 5-11). Barrow (2017) explained that a decrease of pH from 6 to 4 would cause P uptake by roots to increase, as well as the amount of P desorbed from soil to increase. At lower soil pH, PO_4^{2-} ions can react with soluble iron and aluminium colloids to form insoluble precipitates that are unavailable to plants (McLaren and Cameron, 1996). Hence, uptake of P by roots and P desorption are likely to be the reason for an increase of Olsen P with a decrease in soil pH. Barrow (2017) additionally found an increase of soluble P in soil above pH 7. Phosphorus concentration was lowest at pH 5.5 to 6.5. Soil pH did not exceed 7.0 in the top 30 cm of soil at the Lake Ellesmere tributaries, so it was unclear whether an increase of Total P and Olsen P would continue above pH 7.0.

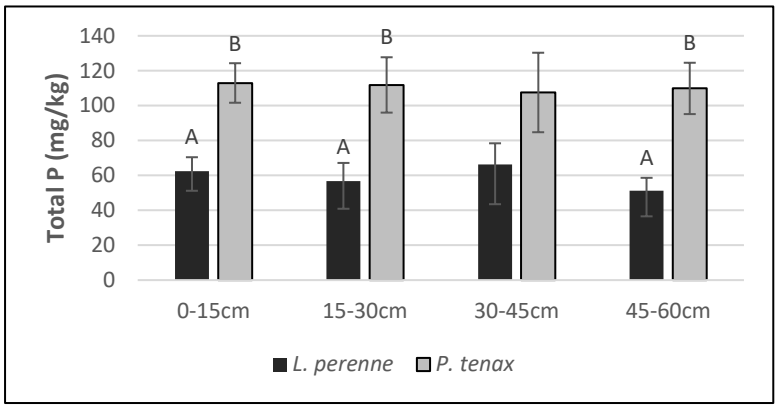


Figure 5-9: Total P concentration at different rhizosphere soil depths of L. perenne & P. tenax at Silver Ferns Farms SFFP. Different letters indicate significant differences between species in each soil depth.

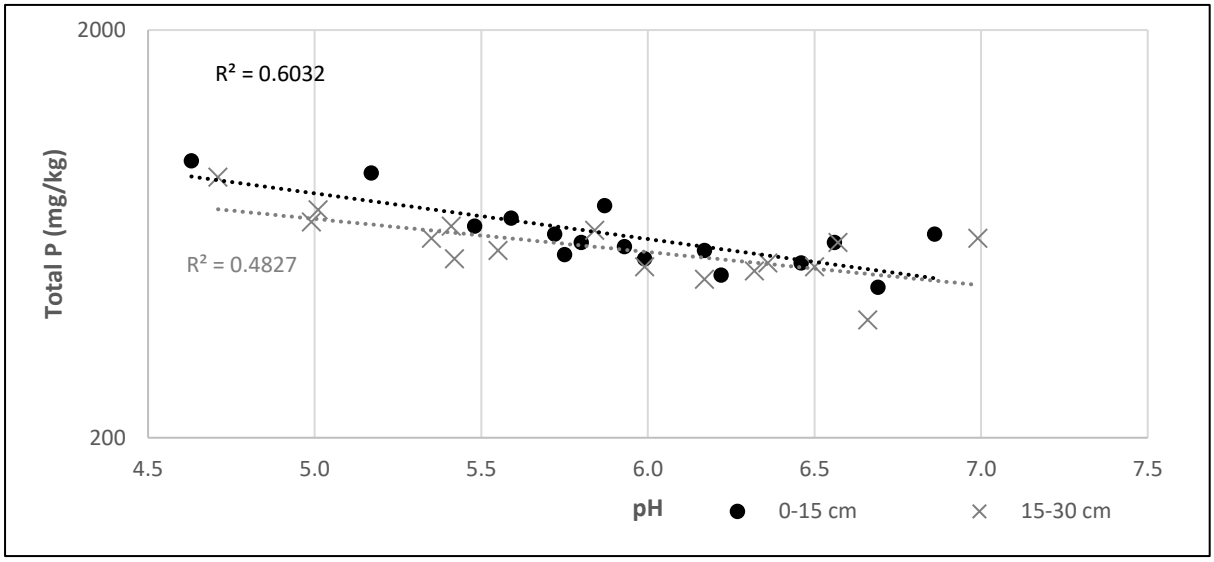


Figure 5-10: Total P concentration (mg/kg) against soil pH in the top 300 mm of soil at the Lake Ellesmere tributaries.

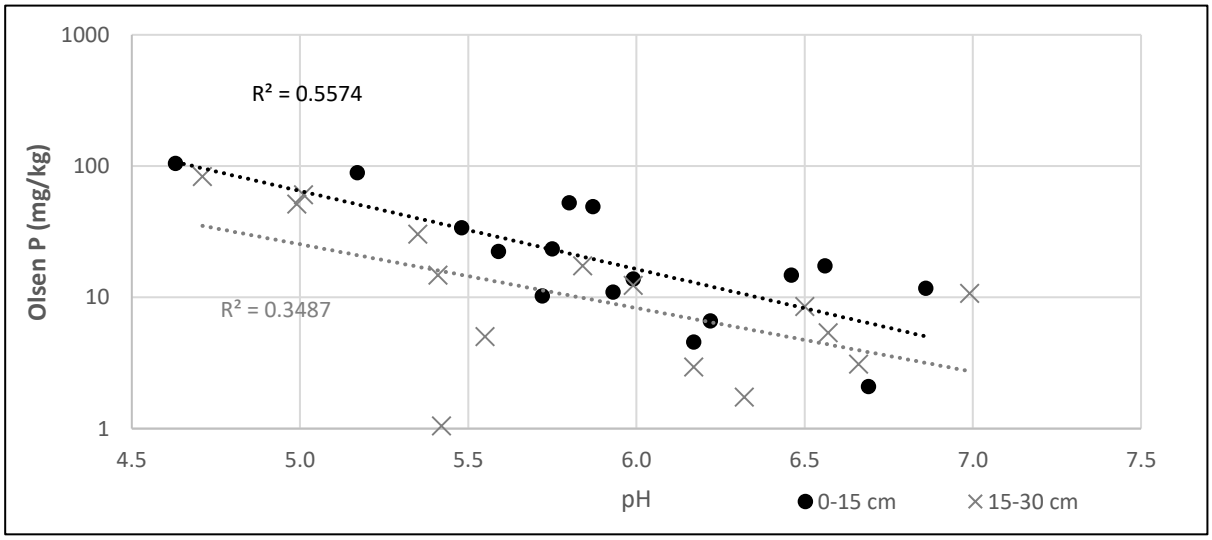


Figure 5-11: Olsen P concentration (mg/kg) against soil pH in the top 300 mm of soil at the Lake Ellesmere tributaries.

5.5. Total Sulphur and Sulphate

Native vegetation had significant effects ($p < 0.05$) on the concentration of total sulphur (TS) and SO_4^{2-} in rhizosphere soil at all sites. At SFFP, concentration of TS was significantly higher in the rhizosphere soil of *P. tenax* compared to *L. perenne* across all soil depths (Figure 5-13). Similar to P, S was added to SFFP paddocks via wastewater application. The total amount that is being removed from *L. perenne* uptake may exceed what is being added to soil. This may explain the lower TS concentration under *L. perenne*. Sulphur cycling in the soil from fallen *P. tenax* foliage will recycle S as microorganisms break-down the plant matter. However, plant available SO_4^{2-} will only account for a small amount of the recycled S, as it will mostly remain as organic S (McLaren and Cameron, 1996).

At Lake Waikare, the concentration of rhizosphere TS under *L. perenne* was significantly ($p < 0.05$) higher than native vegetation (Figure 5-12). Rhizosphere TS did not differ between native vegetation, likely due to the young age of plants. Native vegetation roots may not have had sufficient time to influence soil chemistry in the rhizosphere compared to bulk soil. The surrounding pasture has been used for dairy farming. The land has been exposed to fertilisers and stock for decades. This may explain why TS under *L. perenne* is significantly higher. This farm has retired dairy farming practices since the time of sampling for this research. There may be an influence to TS concentrations in future years in the rhizosphere of *L. perenne*, as fertiliser will not be added to this pasture.

At the Lake Ellesmere tributaries, concentration of TS significantly ($p < 0.05$) varied between native vegetation and pasture, at all depths except for 0-15 cm (Figure 5-14). There were insufficient rhizosphere samples from under *L. scoparium* and *C. robusta* to calculate the standard error (which requires at least three samples). Therefore, they cannot be compared to other native vegetation. TS concentration under *P. tenax* was significantly higher than *L. perenne* and *P. eugenioides*. Rhizosphere soil under *K. robusta* had significantly higher TS concentrations than *L. perenne* and *P. eugenioides* from 15 - 45 cm and 30 – 60 cm, respectively. Rhizosphere soil under *P. eugenioides* was similar to *L. perenne*. Soil TS decreased with an increase of soil depth.

At SFFP, *P. tenax* had a significant effect ($p < 0.05$) on rhizosphere SO_4^{2-} concentration at 15-30cm & 30-45cm. Sulphate concentrations in rhizosphere soil were 2.5-fold lower under *P. tenax* than *L. perenne* (Figure 5-15). Sulphate is soluble and therefore has a high leaching potential (McLaren and Cameron, 1996). However, similar to the PO_4^{2-} fixation processes, SO_4^{2-} has the potential to form less soluble precipitates in acidic soils or can be adsorbed to soil particles in basic soils (McLaren and Cameron, 1996). Phosphorus has a higher absorption potential to SO_4^{2-} and will therefore preferentially bind to soil particles (Metson and Blakemore, 1978). Therefore, the concentration of PO_4^{2-} in soil will influence the concentration of SO_4^{2-}. However, Olsen P concentration did not differ

significantly between *L. perenne* and *P. tenax* at SFFP. Therefore, Olsen P would not have influenced the SO_4^{2-} concentration. Eriksen (1997) found the addition of fertiliser S to *L. perenne* increased SO_4^{2-} periodically, before concentrations lowered again after plant uptake, leaching and conversion to organic S. On top of the wastewater being applied to pasture, SFFP report the application of S and lime to assist in Na accumulation (Conway et al., 2018). Prior to sampling, S fertiliser may have been applied, increasing the concentration of SO_4^{2-} under *L. perenne.*

At the Lake Ellesmere tributaries, SO_4^{2-} concentration in rhizosphere soil under *P. tenax* and *K. robusta* was significantly higher ($p < 0.05$) than *L. perenne* and *P. eugenioides. P. tenax* was significantly higher at all depths whereas *K. robusta* was significantly higher at all depths except for 0-15cm. *P. eugenioides* was similar to *L. perenne* at all depths (Figure 5-16). On average, SO_4^{2-} was five-fold higher under *P. tenax* and *K. robusta* than other species at the Lake Ellesmere tributaries. Sulphate concentrations in the rhizosphere soil of *P. tenax* were higher than *L. perenne*; the opposite was observed at SFFP. This supports the theory that the addition of wastewater and S fertiliser to *L. perenne* at SFFP has increased the concentration of SO_4^{2-}. The trends of lower SO_4^{2-} concentrations of *L. perenne* and *P. eugenioides* mirror those observed for TS in Figure 5-14. Sulphate and TS in rhizosphere soil at the Lake Ellesmere tributaries were significantly correlated across all soil depths. Therefore, at higher concentrations of TS, a higher concentration of SO_4^{2-} is expected.

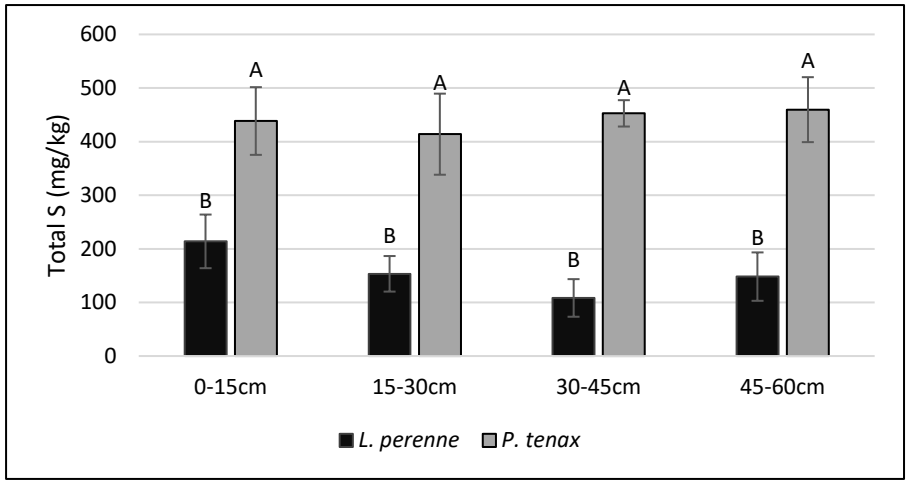


Figure 5-13: Total sulphur concentration (mg/kg) at different rhizosphere soil depths of L. perenne & P. tenax at SFFP

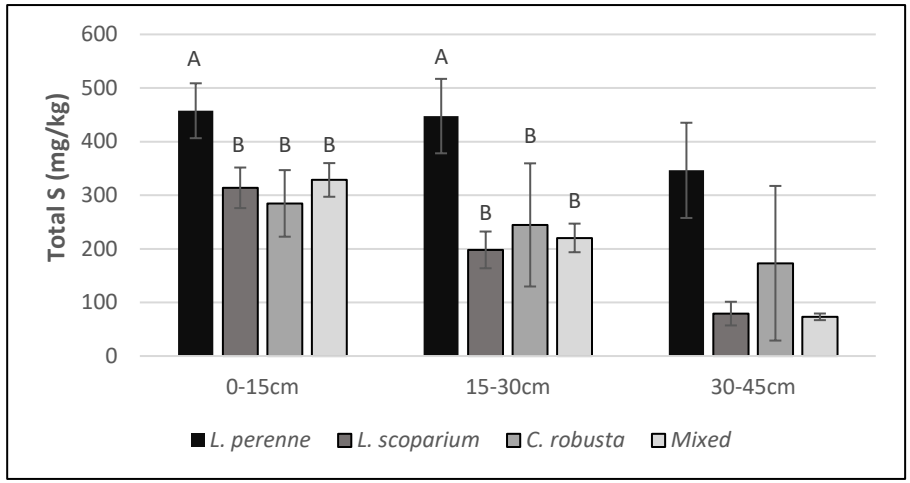


Figure 5-12: Total sulphur concentration (mg/kg) at different rhizosphere soil depths of L. perenne & native species at Lake Waikare.

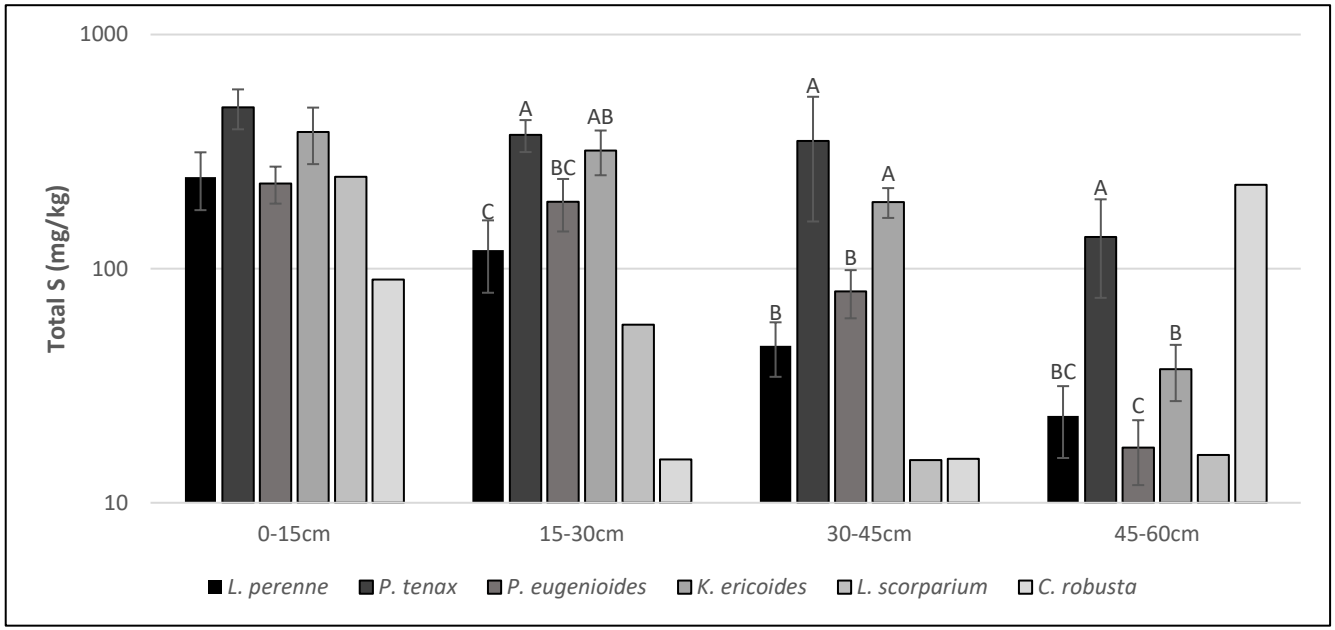


Figure 5-14: Total sulphur concentration (mg/kg) at different rhizosphere soil depths of L. perenne & native species at the Lake Ellesmere tributaries

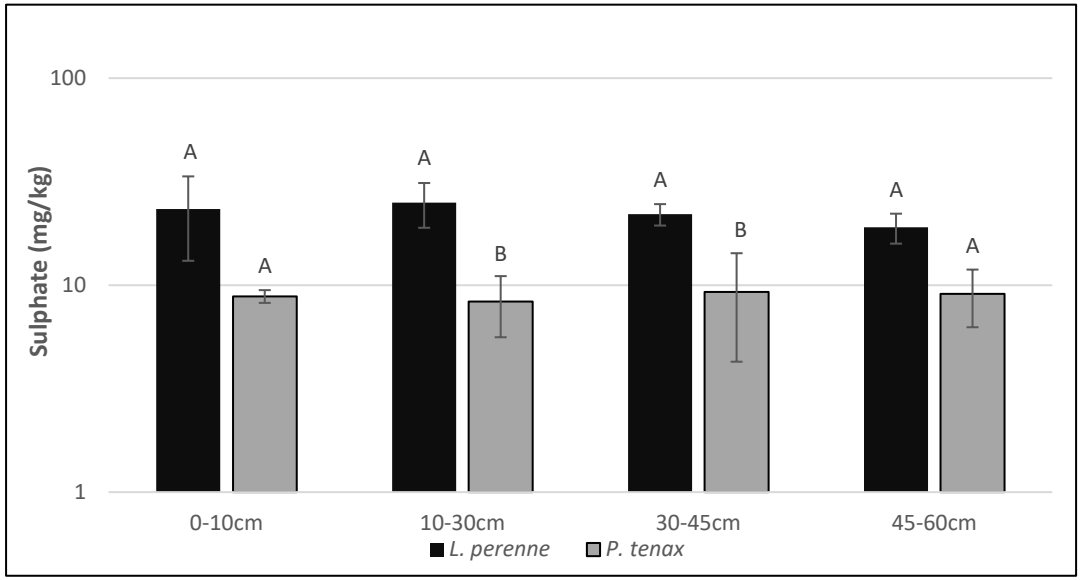
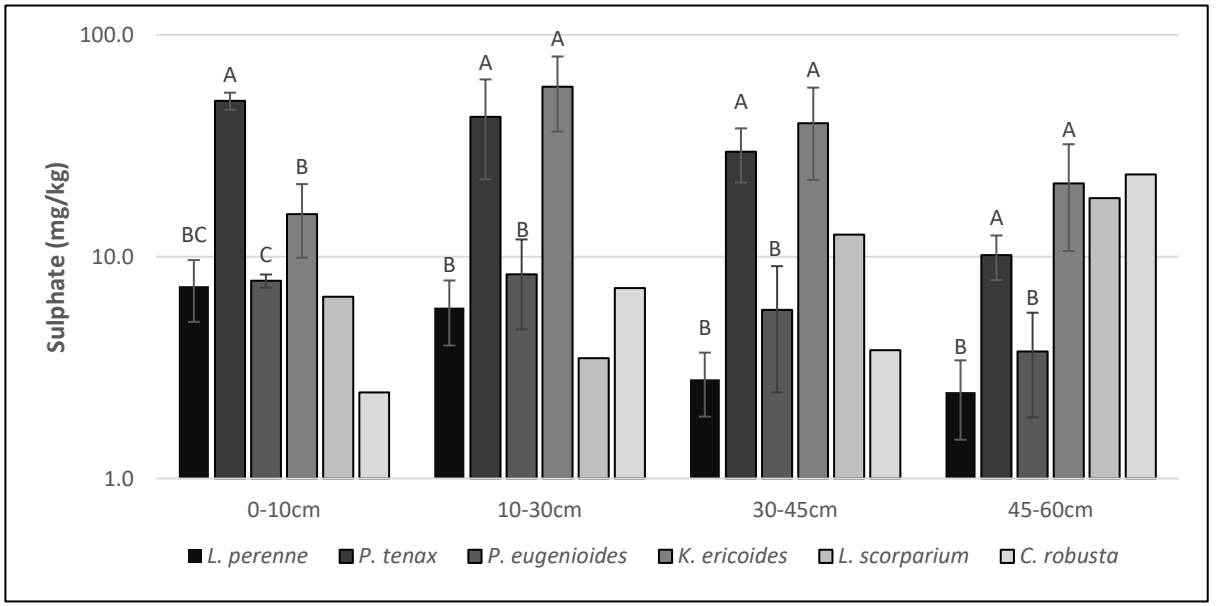


Figure 5-15 (left): Sulphate concentration (mg/kg) at different rhizosphere soil depths of L. perenne & P. tenax at SFFP.

Figure 5-16 (right): Sulphate concentration (mg/kg) at different rhizosphere soil depths of L. perenne & native species at the Lake Ellesmere tributaries.



At the Lake Ellesmere tributaries, TS and SO_4^{2-} had a significant negative correlation with pH in the top 30 cm of soil (Figures 5-17 & 5-18). Total S may be higher at lower pH. Acidic soils have a higher content of Fe and Al cations (McLaren and Cameron, 1996). Sulphate will form precipitates with iron and aluminium at lower pH, potentially contributing to higher concentrations of TS (McLaren and Cameron, 1996). Ghani et al. (1991) and Pirela and Tabatabai (1988) have both recorded the negative correlation of pH and SO_4^{2-}. Ionic SO_4^{2-} does not bind as strongly to soil particles as PO_4^- (Eriksen, 1997; McLaren and Cameron, 1996). Therefore, when in competition with PO_4^{2-}, with lower amounts of cationic exchanges sites at lower pH, PO_4^- will preferentially bind, releasing SO_4^{2-} back into the soil-solution phase.

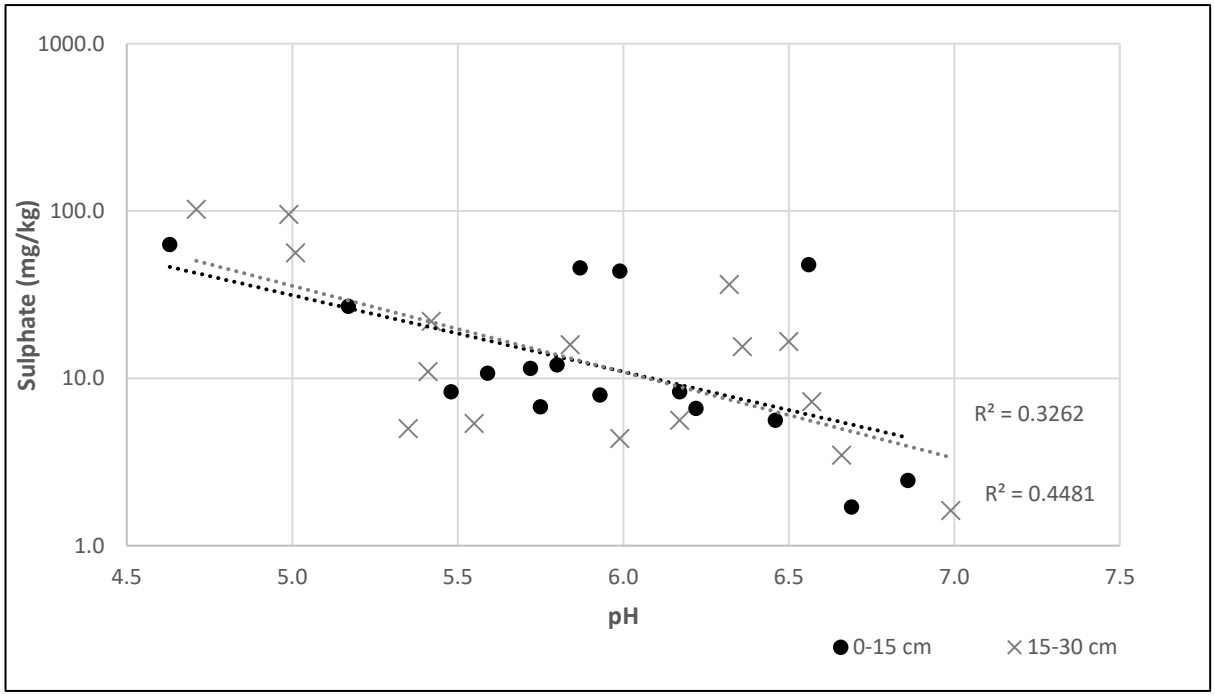


Figure 5-17: Sulphate concentration (mg/kg) against soil pH in the top 300 mm of soil at the Lake Ellesmere tributaries.

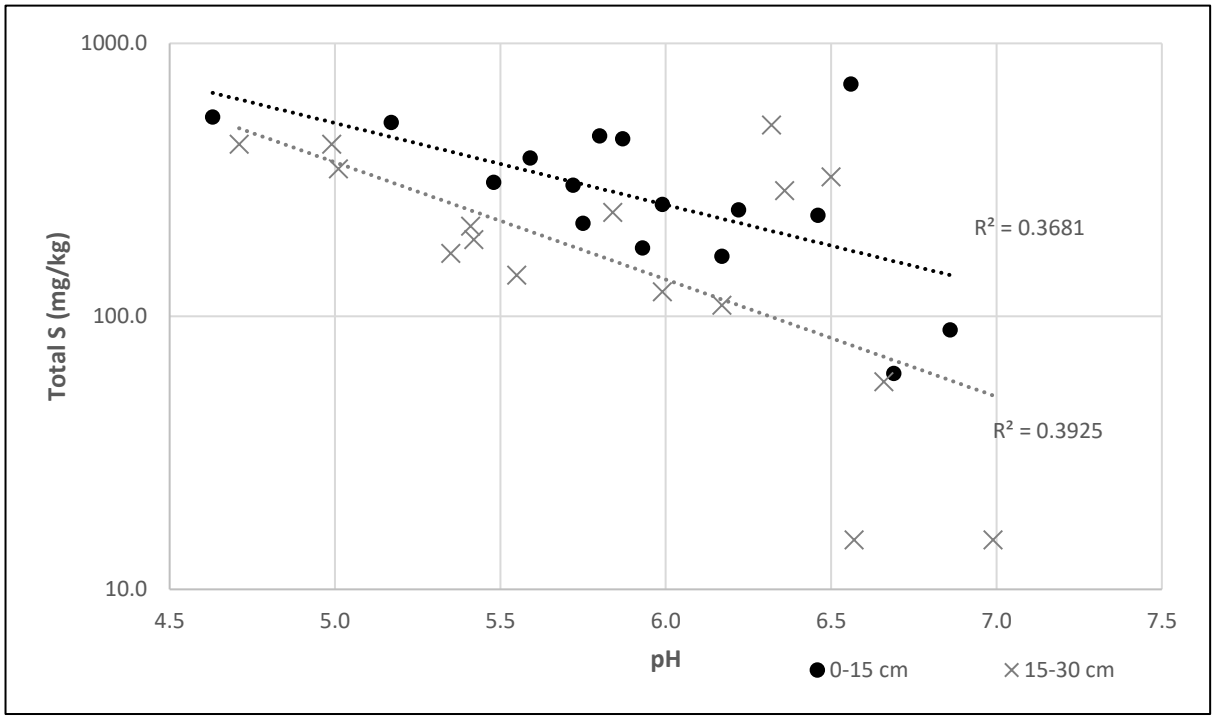


Figure 5-18: Total S concentration (mg/kg) against pH in the top 300 mm of soil at the Lake Ellesmere tributaries.

5.6. Sodium

Sodium was the only other element to have significant differences in the rhizosphere concentration at any of the sampling sites. Native species had both significantly ($p<0.05$) lower and higher rhizosphere concentrations at SFFP and the Lake Ellesmere tributaries, respectively, at depths of 0-15 cm and 15-30 cm. At SFFP, Na concentration in rhizosphere soil of *L. perenne* was significantly higher than *P. tenax* (Figure 5-19). The average concentration of Na across all soils depths under *L. perenne* from my analysis was some 350 mg/kg. The average concentration reported by SFFP was less, with an average of some 250 mg/kg (Conway et al., 2018). This difference may be due to the time of sampling, or analytical techniques used to collect the results. The wastewater applied to pasture at SFFP contains high concentrations of salt. SFFP management said this is due to the salting process of fur pelts in production. This indicates why Na concentration was higher under *L. perenne* than *P. tenax*. At the Lake Ellesmere tributaries, Na concentration of *P. tenax* in rhizosphere soil from 0 - 30 cm was significantly ($p < 0.05$) higher than *L. perenne* (Figure 5-20). This further confirms that wastewater at SFFP has raised Na concentrations under *L. perenne*. At both sites, the standard error increased with increased soil depths. Comparisons at these depths could not be made due to the large standard error values.

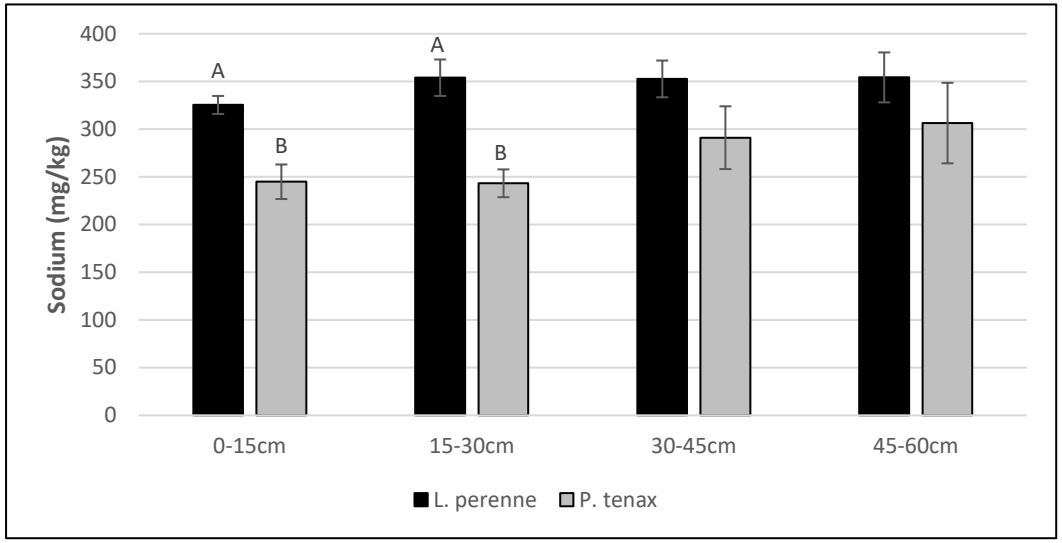
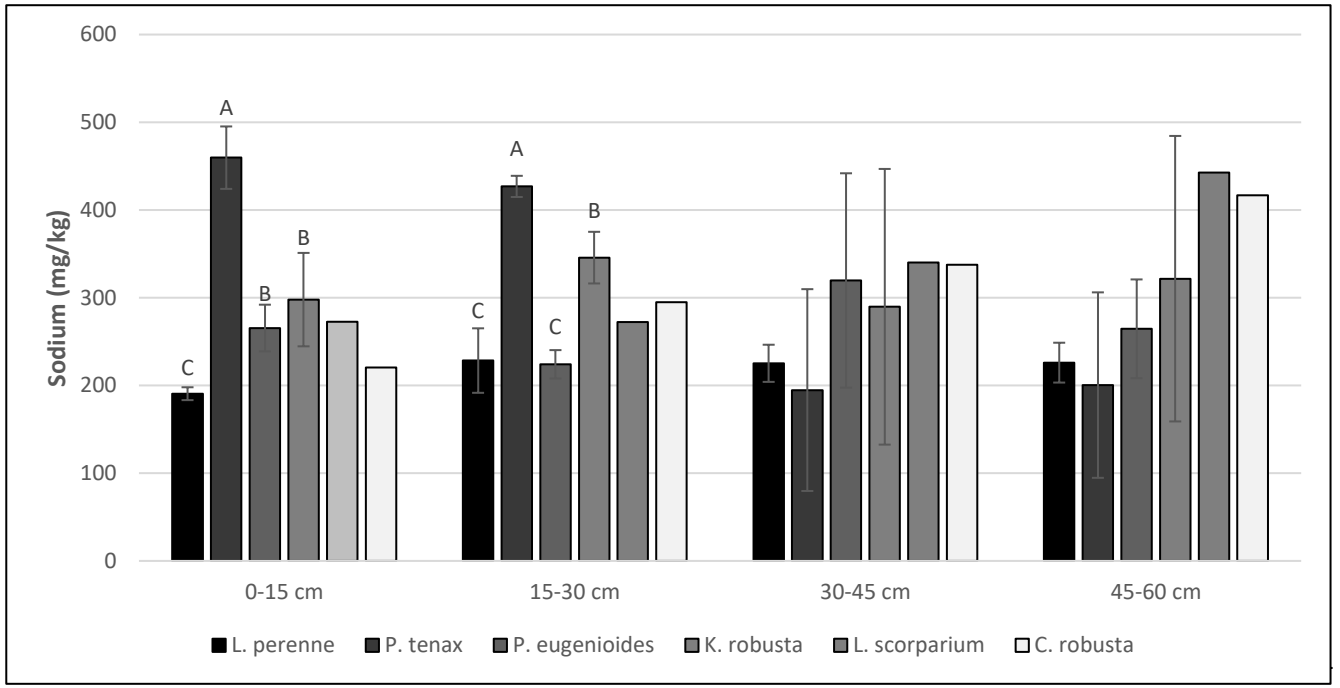


Figure 5-19 (left): Sodium concentration in the rhizosphere of L. perenne and P. tenax at SFFP.

Figure 5-20 (right): Sodium concentration in the rhizosphere of L. perenne and native vegetation across different soil depths at the Lake Ellesmere tributaries.



6. General Discussion

This study did not find large differences in the rhizosphere chemistry between native species used in riparian plantings. There were no significant differences of TN, NO_3^-, NH_4^+, TP and Olsen P in rhizosphere soil, the main drivers of water quality degradation. Only TS, SO_4^{2-} and Na exhibited significant differences in rhizosphere soils at each sampling site. However, these significant differences were insufficient to demonstrate that native vegetation roots were responsible for the changes in TS and SO_4^{2-} concentration. Therefore, this study does not falsify the null hypothesis that there is no difference between NZ-native plant species when considering their effect on the concentration and speciation of N, P and other essential nutrients in soils adjacent to waterways. The results for N-species were consistent with Hahner et al. (2014), who reported no difference in rhizosphere NO_3^- concentration between six native species. However, Hahner et al. (2014) found significant differences of TP and TS between *L. perenne* and native species. Chemical concentrations of TP and TS were on average 20 % and 10 % higher under *L. perenne* than native species, respectively. The difference in chemical concentration of TS and TP is likely because of how the land adjacent to the riparian zone was used. The land adjacent to the native species was used for dairy farming and had been exposed to fertiliser use. Native plant species sampled by Hahner et al. (2014) were five years in age. At SFFP and Lake Ellesmere tributaries, plants were more than five years in age. When there was a significant difference of TP and TS at these sites, this research found that native species generally had higher TP and TS concentrations than *L. perenne*. However, at Lake Waikare, TS concentration under native plants, which were only two years in age, was lower than *L. perenne*. This indicates that the age of native plants may be a factor that influences chemical concentration in rhizosphere soil. Moreover, the results from this study were inconsistent with Franklin et al. (2015), who found significant differences in mineral N concentrations in the rhizosphere of different native vegetation from pot trials. The inconsistency is likely due to differences in field trials and pot trials. With field trials, there are more unknown variables and soils are exposed to more changing conditions than pot trials. This increases that difficulty to interpret why there may or may not be significant differences in rhizosphere concentrations between native species.

The results from this study indicate that soil heterogeneity between sampling sites results in large differences in chemical concentration and speciation. Soil heterogeneity originates from differences in factors such as climate, parent material, land use, native vegetation selection and native vegetation concentration. While soil heterogeneity would occur in pot trials, the changes between soil characteristics will not be as significant as field studies. However, planting a diversity of vegetation

species is essential for the best management of chemical fluxes in heterogeneous soils. While some native species have been propounded for managing specific chemical fluxes better than others (Dollery et al., 2019; Franklin, 2014; Franklin et al., 2015), this research has indicated that there are insignificant differences between the native species tested. This does not imply that all NZ-native species perform equally. This study investigated the chemical speciation in the rhizosphere of five native species, there may be important physical and antimicrobial differences between species that have not been investigated in this research.

Hahner et al. (2014) reported considerable interspecific variability in roots structures of NZ-native species. These differences would affect infiltration rate, the distribution of root exudates, soil physicochemical properties, soil microbial activity and the solubility of nutrients. Higher infiltration rates may increase the leaching of chemicals (i.e. NO_3^-). Many NZ-native species have shallow roots, confined to the top 30 cm of soil (Marden et al., 2007). This reduces their capacity to stabilise soil next to larger river systems. Consequently, PO_4^{2-} or SO_4^{2-} bound to soil particles may not be intercepted, as sediments are eroded. However, smaller river systems, native vegetation may stabilise soils effectively to intercept chemicals from entering freshwater bodies (Marden et al., 2007). Assuming that native species are spaced evenly, wider riparian zones may have better soil stabilising properties than narrower riparian zones due to a higher quantity of plants. A question that arises from this study is: how wide do riparian buffer strips need to be in order to protect the surrounding freshwater from contaminants? As mentioned in the background, a 7,500 m^2 area of diverse native plantings would cost an estimated NZ$150,000 (MPI - Stock exclusion costs report 2016). On top of planting costs, there are additional costs to the farmer; the forfeit of productive land and ongoing maintenance costs make the introduction of a riparian zone an expensive procedure. The scope of this research did not include the determination of the ideal width of a riparian zone. There was insufficient data to begin this process. However, the riparian zones in my study, ranging from 2 m to 20 m, showed no significant differences between N & P concentration and speciation of rhizosphere soil in these areas. This was inconsistent with Fennessy and Cronk (1997), who found that riparian buffers that were 20-30 m in width removed up to 100% of NO_3^-. However, that study did not include NZ native vegetation. The objective of this research was to determine any chemical differences between native vegetation, not to suggest an ideal width zone for riparian planting. The evidence points to wider buffer zones of NZ native riparian plantings for better contaminant management, as there is reduced soil erosion and better stock exclusion. However, the costs to farmers may prohibit wider riparian zone planting. Further studies should look at the physical transportation of chemicals and sediments in riparian zones, to characterise a riparian width zone that is optimised for environmental benefits and associated financial costs.

A wider riparian zone will provide improved environmental conditions for native fauna (Parkyn et al., 2000). A wider riparian buffer may be economically feasible, if there are methods to offer commercial value or have alternative incentives to reduce the large initial costs. The production of mānuka honey is a viable commercial option for riparian zones. Mānuka is a highly sought after food commodity, due to its natural antimicrobial and antioxidant properties (Adams et al., 2009; Alvarez-Suarez et al., 2014). There are many factors when evaluating the estimated earnings from producing Mānuka Honey. For example: market value of honey, quantity of mānuka plants, quantity of bee hives, productivity of hives and quality of honey (MPI - Apiculture 2018b). From 2013 to 2018, mānuka honey exports have resulted in some $1.5 billion of export earnings (MPI - Apiculture 2018b). The number of registered bee hives in NZ have doubled from some 450,000 to almost 900,000 during the period of 2013 to 2018. Bulk honey prices per kilogram have similarly doubled in price during the period (MPI - Apiculture 2018b). This has been driven by the strong overseas market demand for mānuka honey. Although mānuka honey does not reduce the large initial costs option, it could provide the farmer with a diverse stream of income, offering an improved future income stability. Tourism could add commercial value to riparian zones (Krukowska and Krukowski, 2013). NZ tourism relies greatly on a pristine and clean environment. Riparian zones can capture the attractive element of the freshwater to land interface, providing a unique experience of the natural environment. Opportunities for commercial value may arise from a required payment or donation at the beginning of the walk. This would not be a primary method for funding the riparian zone, rather another small method of compensating costs. An option can be that groups planning to plant native riparian zones seek funding and/or grants. There are grants available to assist landowners with options for planting native vegetation. For example, the One Billion Trees Fund has offered $240 million in grants and funding to landowners, organisations and communities who want to plant more trees (MPI - One billion trees programme 2020). For the most part, funding for native vegetation is a case-to-case basis due to how specific the conditions of each site are. The correct native species, count and distribution of vegetation must be put in place for each planting project. There may be an opportunity for extra funding or grants from different industries or communities. Riparian zones are known to provide several benefits to freshwater environments (Lee et al., 2003; Pan et al., 2011; Pusey and Arthington, 2003). This would eventually benefit freshwater fishing, as riparian planting offers improved habitats for fish species (Crook and Robertson, 1999; Everett and Ruiz, 1993). The freshwater fishing industry could offer funding or grants to farmers to provide riparian zones that will environmentally improve the conditions of adjacent freshwater, improving the opportunity for commercial or recreational fishing.

7. Conclusion

In the root-zones of NZ-native species, there were insignificant interspecific differences in the concentration and speciation of N & P. Therefore, the null hypothesis for this research cannot be rejected. Additional research must be completed to develop the understanding of how each species interacts with contaminants in contrasting soil types. This research has shown that:

- There were no significant differences in the rhizosphere concentrations of total N, NO_3^- and NH_4^+ between *Phormium tenax, Kunzea robusta, Leptospermum scoparium, Coprosma robusta* and *Pittosporum eugenioides* at SFFP, Lake Ellesmere tributaries and Lake Waikare sites. These elements were significantly correlated with pH, however the sign of the correlation (negative or positive) was site dependent.
- As with N, there were no significant interspecific differences in the concentrations of TP & Olsen P. However, TP was affected by cut-and-carry of *Lolium perenne* at SFFP.
- TS and SO_4^{2-} had significantly different rhizosphere concentrations between native species. TS concentration under *P. tenax* and *K. robusta* was significantly higher than *L. perenne* at SFFP and Lake Ellesmere. However, while SO_4^{2-} concentration under *P. tenax* and *K robusta* was higher than *L. perenne* at Lake Ellesmere, *P. tenax* was lower than *L. perenne* at SFFP. The results showed that TS and SO_4^{2-} concentration under *P. tenax* and *K. robusta* was generally higher than *L. perenne. Leptospermum scoparium, Coprosma robusta* and *Pittosporum scoparium* showed no significant differences between TS and SO_4^{2-}.
- Soil pH and TC were not significantly influenced by different native species. This could be due to different cycling processes.
- Soil properties, rather than native species were the overriding importance in affecting the concentration of speciation of N, P & S in the root-zone. For example, decreasing depth of concentration in TN with increased soil depth.
- The lack of interspecific differences at Lake Waikare in this study may be due to the age of the plants being less than three years of age.

The lack of differences does not indicate that NZ-native plant species selection is not important in riparian plantings: water quality is also a function of other factors, such as antimicrobial activity and increased infiltration, which were not measured in this study. Species selection should also be informed by ecological and farm management requirements.

7.1. Recommendations for Further Research

The key finding of this research is that there were negligible differences in the chemical speciation of N & P in the rhizosphere of five NZ native species. However, this does not imply that species selection is unimportant for riparian planting.

Other biological and physicochemical soil parameters

There was a range of biological (e.g. microorganism diversity, count and species), physical (e.g. soil water capacity, oxygen availability and soil temperature) and chemical (cation exchange capacity) parameters that this study did not evaluate. This study focused on chemical concentration and speciation of essential nutrients. Other parameters, such as microorganism diversity, cation exchange capacity and oxygen availability may reveal differences in nutrient speciation under specific plants. Additional parameters would reduce the uncertainty that arises from completing field trials. Heterogeneity of soils across different sampling sites is difficult to characterise, but these additional parameters would bring a better context to the overall picture of chemicals moving through soil in native riparian zones.

Nutrient Cycling

Complex factors such as transpiration, leaf litter decomposition, soil leaching rates and microbial community control the cycling of nutrients. Characterisation of these complex factors would better show the influence of native roots on chemical concentration and speciation. This will give total mass balance for riparian and/or pasture land, quantifying the inputs and outputs of nutrients.

Soil types

This research only looked at chemicals in fragic pallic and orthic gley soils. There are 15 main categories of soil orders in NZ (Hewitt and Dymond, 2013). They are ordered based on factors during their formation such as: age, climate, wetness and parent rock type. Each factor during the soil formation process will give different chemical, physical and biological properties to the soil (Hewitt and Dymond, 2013). Collectively, the semiarid, pallic, brown and podzol order soils make over 73% of total soils in NZ. Future studies should consider the soil type when looking at how native vegetation influences chemical concentration and speciation. Soil type can be important for GSMC, SMC and oxygen availability as recorded in this research.

Variety of Native Species

Future work should consider looking at a wider scope of native vegetation. The goal of this research is to contribute further towards the understanding of how native vegetation interacts with chemical

concentration and speciation so that farmers, catchment groups and councils can more efficiently use financial resources to establish native vegetation in riparian zones. A wider variety of native vegetation will provide the opportunity to open up a larger collection of vegetation diversity for stakeholders.

Seasonality effects

Seasonality can affect physicochemical factors such as soil moisture content, oxygen availability and temperature, which can lead to changes in pH and microorganism composition and availability. Olarewaju et al. (2009) found a 14% decrease of NO_3^- in wet seasons compared to dry seasons. Other important nutrients such as P or S have no record of seasonality effect in the rhizosphere of NZ native plants.

Age of plants

It was evident that the age of plants had an influence of soil chemistry in rhizosphere soil. At Lake Waikare, plants had only been planted two years prior to sampling. The results showed consistent nutrient concentrations between native vegetation. At the other sites, vegetation had had longer to influence soil chemistry in the rhizosphere.

Other forms of N loss

This project only looked at N loss via leaching in the form of NO_3^-. This is not the only form of N loss during the N cycle. Firstly, it would be important to further characterise the individual root stability properties of native vegetation. This would be useful when predicting P contamination of freshwater bodies through sediment displacement. Sediment would also carry soil bound N. Gaseous losses from denitrification are important to consider. Particularly, N_2O due to its adverse impacts on global warming and the ozone layer. Esperschuetz et al. 2017 Esperschuetz et al. (2017b) reported that *L. scoparium* and *K. robusta* were better at reducing N_2O emissions. Although denitrification does not directly impact freshwater quality, which was what this project examined, it is still an important environmental consideration to evaluate the impact to the atmosphere.

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Appendices

Appendix 1: Tables for all chemical parameters measured in soil 30 -45 cm and 45 – 60 cm

Table 7-1: Means (and standard error ranges) of the chemical parameters analysed between 30 - 45 cm of soil at each sampling location. The units for all data is mg/kg unless otherwise stated in brackets. Results that are significant have different letters to represent this.
**Geometric mean calculated with the standard error range.*

30-45cm	**Pareora**		**Lake Waikare**				**Lake Ellesmere Tributaries**			
Chemical	*L. perenne*	*P. tenax*	*L. perenne*	*L. scoparium*	*C. robusta*	*Mixed (L. scoparium)*	*L. perenne*	*P. tenax*	P. eugenioides	K. robusta
pH*	6.3 (6.0 - 6.8)	6.5 (6.4 - 6.6)	7.0 (6.9 - 7.1)	6.3 (6.1 - 6.6)	6.6 (6.5 - 6.7)	6.7 (6.6 - 6.9)	6.1 (5.9 - 6.3)	6.0 (6.0 - 6.1)	5.8 (5.6 - 6.0)	5.7 (5.4 - 6.3)
NO_3^-	0.6 ± 0.2	2.1 ± 1.1	2.2 ± 1.0	2.1 ± 0.7	0.3 ± 0.1	1.8 ± 0.7	0.8 ± 0.5	2.3 ± 1.6	0.8 ± 0.2	2.2 ± 1.0
NH_4^+	1.7 ± 0.7	2.1 ± 0.9	1.7 ± 0.4 [a]	3.5 ± 0.9 [a]	0.4 ± 0.1 [b]	3.5 ± 1.4 [a]	3.4 ± 2.4	6.5 ± 3.8	2.2 ± 0.7	4.4 ± 1.3
Total N (%)	0.06 ± 0.01	0.09 ± 0.03	0.10 ± 0.02	0.13 ± 0.03	0.07 ± 0.01	0.10 ± 0.01	0.08 ± 0.02	0.34 ± 0.14	0.15 ± 0.02	0.24 ± 0.01
Total C (%)	0.47 ± 0.14	0.85 ± 0.3	1.06 ± 0.21	1.52 ± 0.39	0.82 ± 0.08	1.12 ± 0.14	0.70 ± 0.24	4.49 ± 2.31	1.50 ± 0.23	2.68 ± 0.16
Olsen P	11.7 ± 7.7	5.4 ± 2.7	5.7 ± 2.7	7.4 ± 2.7	1.2 ± 0.7	4.8 ± 0.7	3.8 ± 1.0	8.4 ± 4.7	4.9 ± 1.4	10.3 ± 3.2
Total P	66 ± 12	108 ± 23	238 ± 35	318 ± 50	252 ± 36	261 ± 25	560 ± 22	572 ± 44	510 ± 35	553 ± 11.3
Sulphate	22 ± 2.6 [a]	9.3 ± 5.0 [b]	6.2 ± 2.8	12.7 ± 3.1	8.4 ± 5.4	8.2 ± 3.9	2.8 ± 0.9 [b]	29.7 ± 8.2 [a]	5.8 ± 3.3 [b]	40.0 ± 17.8 [a]
Total S	108 ± 35 [b]	453 ± 25 [a]	346 ± 89	79 ± 22	173 ± 144	73 ± 6.2	47 ± 12 [b]	351 ± 192 [a]	80 ± 19 [ab]	193 ± 28 [a]
Total K	1477 ± 215	1215 ± 234	609 ± 57 [a]	645 ± 60 [a]	482 ± 24 [b]	533 ± 22 [ab]	2198 ± 34	1917 ± 316	2579 ± 141	2811 ± 289
Cu	3.3 ± 1.8	3.3 ± 1.0	5.7 ± 0.6	6.0 ± 0.7	6.2 ± 2.9	5.7 ± 1.1	7.5 ± 2.3	7.5 ± 1.6	6.4 ± 0.2	9.5 ± 0.9
Fe	13600 ± 1100	10800 ± 2100	23300 ± 3000	26500 ± 3400	21600 ± 1600	21000 ± 3400	23000 ± 900	24900 ± 3800	22900 ± 1100	24400 ± 340
Mg	4360 ± 1070	2920 ± 900	10300 ± 1040	13600 ± 1740	10100 ± 470	11000 ± 1940	15000 ± 450	16100 ± 2060	15100 ± 600	16200 ± 80
Mn	354 ± 155	331 ± 78	206 ± 61	210 ± 94	82 ± 36	250 ± 73	428 ± 32	417 ± 77	511 ± 103	473 ± 24
Zn	2.6 ± 1.2	2.8 ± 1.3	3.3 ± 1.6	3.9 ± 1.8	3.2 ± 1.6	7.4 ± 0.5	3.2 ± 1.9	11.4 ± 6.4	2.3 ± 1.8	10.8 ± 10.3
Na	353 ± 19	291 ± 61	125 ± 10	149 ± 17	187 ± 26	151 ± 6	225 ± 21	195 ± 115	320 ± 122	290 ± 157
Ca	3270 ± 210	3220 ± 590	3330 ± 880	6230 ± 3530	1190 ± 130	2370 ± 470	6220 ± 400	8090 ± 690	6120 ± 340	7020 ± 300

Table 7-2: Means (and standard error ranges) of the chemical parameters analysed between 45 - 60 cm of soil at each sampling location. The units for all data is mg/kg unless otherwise stated in brackets. Results that are significant have different letters to represent this.
**Geometric mean calculated with the standard error ranges.*

45-60cm	**Pareora**		**Lake Ellesmere Tributaries**			
Chemical	*L. perenne*	*P. tenax*	*L. perenne*	*P. tenax*	P. eugenioides	K. robusta
pH*	6.2 (5.9 - 6.6)	6.4 (6.3 - 6.7)	6.5 (6.4 - 6.8)	6.8 (6.6 - 7.1)	6.0 (5.8 - 6.3)	6.5 (6.2 - 7.4)
NO_3^-	0.6 ± 0.3	1.5 ± 0.6	0.5 ± 0.2	0.3 ± 0.1	0.4 ± 0.2	1.2 ± 0.6
NH_4^+	1.0 ± 0.4	1.5 ± 0.6	0.4 ± 0.3	5.5 ± 2.4	0.7 ± 0.1	1.4 ± 0.7
Total N (%)	0.05 ± 0.01	0.08 ± 0.03	0.06 ± 0.02	0.15 ± 0.03	0.07 ± 0.01	0.08 ± 0.02
Total C (%)	0.37 ± 0.06	0.78 ± 0.44	0.49 ± 0.22	1.66 ± 0.49	0.69 ± 0.11	0.83 ± 0.25
Olsen P	13 ± 8.9	9.2 ± 6.0	2.5 ± 0.8	4.6 ± 1.5	2.0 ± 0.7	1.5 ± 0.3
Total P	51 ± 7 B	110 ± 15 A	550 ± 42	536 ± 8	495 ± 58	532 ± 45
Sulphate	19.0 ± 3.1	9.1 ± 2.8	2.5 ± 1.0 B	10.2 ± 2.3 A	3.7 ± 1.9 B	21.4 ± 10.8 A
Total S	148 ± 45 B	460 ± 61 A	24 ± 8 B	136 ± 61 A	17 ± 5 B	37 ± 10 AB
Total K	1583 ± 211	1337 ± 118	2158 ± 222	1974 ± 146	2208 ± 246	2323 ± 146
Cu	4.0 ± 1.4	4.3 ± 1.5	8.4 ± 1.8	10.0 ± 0.2	8.1 ± 0.6	11.8 ± 1.3
Fe	12800 ± 490	11900 ± 840	22100 ± 1000	23300 ± 770	23300 ± 930	25000 ± 1600
Mg	4300 ± 1350	4000 ± 650	14600 ± 780	15500 ± 490	15500 ± 540	16500 ± 920
Mn	139 ± 7 B	359 ± 66 A	371 ± 14	359 ± 61	433 ± 83	454 ± 27
Zn	2.3 ± 1.8	1.0 ± 0.5	1.5 ± 1.0	3.3 ± 2.8	0.5 ± 0.1	1.1 ± 0.6
Na	354 ± 26	306 ± 42	226 ± 23	200 ± 106	265 ± 56	322 ± 163
Ca	3140 ± 160	3140 ± 200	5920 ± 230	7090 ± 570	6310 ± 410	7240 ± 370