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The potential of native plants to manage nutrient and contaminant fluxes from New Zealand dairy farms

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Natural Resources Management and Ecological Engineering (M.Na.R.M.&E.E.) at Lincoln University by J.L. Hahner

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Abstract of a thesis submitted in partial fulfillment of the requirements for the Degree of M.Na.R.M.&E.E.

The potential of native plants to manage nutrient and contaminant fluxes from New Zealand dairy farms

By

J.L. Hahner

This study investigates the elemental composition of components from the soil-plant continuum of 6 New Zealand native plant species. These components have been evaluated to determine if the plants have potential uses in trace element management and if there are any potential capabilities of these plants to attenuate contaminant flux from soil and soil leachate resulting from New Zealand dairy paddocks. Plants were selected based on their compatibility with riparian plantings, root morphology, plant structure and physiological traits. An initial investigation included collection and analysis of vegetation, soil and rhizon soil leachate samples from each sample site to collect baseline data.

New Zealand native plant species are found to have distinct patterns of elemental accumulation when comparing native monocots and dicots as well as to exotic ryegrass. Foliage concentrations of N, P, K and S were highest in ryegrass (L. perenne), although significant differences between native plant species were found. Foliage concentrations of Cd were up to 10 fold higher in native plant species when compared to ryegrass. Significant differences in elemental concentrations were found between the soils of the paddock margin and adjacent intensively managed paddock soils.
Dairy cattle effluent was then applied to the soil surface adjacent to each plant at a volume equivalent to 50 kg N ha\(^{-1}\). Soil leachate samples were collected for a period of one month following the effluent application to evaluate the influences of each plants rhizosphere on the leaching of the effluent through the soil profile.

Significantly higher concentrations of nitrate were found beneath *C. richardii*. However, differences found in soil leachate chemistry may be attributed to differences in plant physiology and root morphology. Soil temperature and moisture had little apparent effect on rhizosphere chemistry over the early spring months. Soluble nitrogen mobility through native plant rhizospheres is probably not a major nitrogen flux pathway. Some native plants exhibit elemental properties that could potentially be suitable as fodder supplements.

Key words: attenuation, dairy, effluent, eutrophication, New Zealand, phytoremediation, rhizon, rhizosphere, riparian
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1. Introduction

1.1 Surface runoff and leaching of contaminants

New Zealand’s Ministry for the Environment recognizes that maintaining a high standard of water quality is essential for sustaining the economic growth, natural environment, cultural heritage and the health and wellbeing of New Zealand’s citizens. The New Zealand government enacted the Resource Management Act (1991) as a key piece of legislation governing the management of freshwater resources. More recent legislation includes the New Start For Fresh Water (MfE, 2009) and the reformed Fresh Start For Fresh Water (MfE, 2011). These directives identify the environmental significance and community interest of protecting our freshwater resources. Managing the leaching of nutrients from agricultural land is a part of this.

The New Zealand dairy industry is one of the nation’s leading industries, bringing in around $5 billion in 2010 (Schilling, Zuccollo, & Nixon, 2010). In Canterbury alone, regional dairy production revenue netted nearly $1 billion in 2009 (Dairy dollars help keep economy healthy, 2010; Schilling et al., 2010). Provisional results from the 2010 Agricultural Production Survey revealed that the total number of dairy cattle in New Zealand was close to 6 million at 30 June 2010, in addition to 3.9 million beef cattle. (Ashley-Jones, 2010).

Dairy cattle effluent has been identified as a source of eutrophication of Canterbury’s surface and groundwater (Monaghan et al., 2008; Monaghan et al., 2007). The livestock populations excrete about 40 times more organic waste than New Zealand’s human population. The treeless pastures are a potential source of surface and sub-surface run-off, washing some of this waste as well as sediment and fertiliser residues into waterways (The state of New Zealands environment 1997, 1997). Effluent that is excreted onto the milking platform is collected into treatment ponds for storage and disposal. Direct discharge of effluent into waterways has become discouraged by the New Zealand government and now requires resource consent (Selvarajah, 1999, as cited in N. Bolan, Khan, Donaldson, Adriano, & Matthew, 2003). The modern and preferred method of effluent disposal is by land
application to the pastures through irrigation systems. Through this method, much of the biological oxygen demand and suspended solids are removed from the effluent. However, when fertilizers or effluent are applied in excessive amounts or under inappropriate conditions, nutrients and other contaminants including metals leach into surface and groundwater causing contamination. Considerable amounts of nitrogen leach from intensively grazed pastures within New Zealand, sometimes as much as 200 kg N ha\(^{-1}\) yr\(^{-1}\) due largely to urine patches (McLaren & Cameron, 1996). Nitrogen in the form of ammonium (NH\(_4^+\)) from urine is largely immobile and protected from leaching due to cation exchange reactions on the surface of clays and organic matter in the soil. However, nitrifying bacteria within the soil can convert ammonium (NH\(_4^+\)) into nitrite (NO\(_2^-\)) and nitrate (NO\(_3^-\)), which because of their negative charge are repelled by cation exchange sites and are then readily leached when water drains through the soil (McLaren & Cameron, 1996). Inorganic fertilizers and animal manure are also major sources of phosphate. The Environmental Protection Agency (EPA) has set maximum levels of 10mg/l nitrates in groundwater and 0.05 mg/l phosphate in a stream that enters a lake or reservoir and total phosphorus is not to exceed 0.1 for the same situation (Sparks, 2003). Phosphorus in the form of phosphate is usually not a threat to groundwater contamination, since it is readily held by soil particles through both electrostatic and non-electrostatic bonds and usually does not leach in most soils. However, in sandy soils with little clay or organic matter, phosphate can leach through the soil and impact groundwater quality (Sparks, 2003). The nutrients stimulate significant levels of aquatic flora and algal growth and result in eutrophication of freshwater resources (N. Bolan et al., 2003; N. S. Bolan, Laurenson, Luo, & Sukias, 2009; N. S. Bolan, Wong, & Adriano, 2004; Magesan, McLay, & Lal, 1998; McLaren & Cameron, 1996; Sparks, 2003, p. 5). The decomposition of dying aquatic plants and algal blooms deplete the water of dissolved oxygen, causing a reduction in fish and other aquatic life (McLaren & Cameron, 1996).

This project investigates the potential role that native plants in riparian zones may play in management of nutrients and trace elements and in remediating runoff from dairy paddocks. Proposed solutions for remediating soil, groundwater and surface water contamination resulting from intensive dairy farming should be effective, affordable and complementary to existing pasture management. An additional benefit of utilizing native
plants for the management of trace elements is their potential use as fodder and supply of nutrient supplements for livestock. Concentrations of trace elements in plants are often positively correlated with the abundance of these elements in the soil (Kabata-Pendias & Mukherjee, 2007) and limited by the ability of the plants to accumulate such elements. Some trace elements such as zinc are essential to animals because it is not stored in the body and must be supplied continuously with the diet (Kabata-Pendias & Mukherjee, 2007). Identifying plant species that could be implemented in paddock margins and are capable of resolving contamination problems would assist resource managers in making more knowledgeable decisions when selecting species for riparian plantings adjacent to agricultural lands.

1.2 Phytoremediation and riparian planting

Of the various contaminant remediation techniques, phytoremediation is acknowledged as being cost-effective and environmentally friendly (Kruger, Anderson, & Coats, 1997). Phytoremediation methods utilize various plants to extract, contain, immobilize or degrade contaminants from soil and water (Singh & Ward, 2004). Utilizing phytoremediation technology within riparian zones produces additional benefits by providing complementary ecosystem services beyond the assimilation of soil contaminants. Mander, Yoshih and Valdo (2005) describe some of the important functions of riparian buffer zones to include filtering of polluted overland and subsurface flows from nearby agricultural areas, protecting banks of water bodies against erosion, filtering polluted air, reducing intensive growth of aquatic macrophytes through shading, improving microclimates, creating new habitats and ecotones, and creating more connectivity in landscapes due to migration corridors and stepping stones. Implementing phytoremediation technology through riparian planting is likely to create a barrier that prevents soil erosion and contaminants that have resulted from farm management actions, from entering surface waters and leading to high levels of suspended solids (Leccce, Pease, Gares, & Wang, 2006; Vigiak et al., 2010). However, there is little evidence to support this within dairy systems in New Zealand or elsewhere. Establishing native plant species along riparian zones also
provides additional potential benefits: it creates a linear habitat that acts as a conduit for organism dispersal. These created environments attract species such as birds, which are in the focus of public interest and care (Markert, Bruer, & Zechmeister, 2003). Replenishing shade across the lowland streams will also improve habitat quality for native fish and reduce the chances of proliferations of algae and introduced weeds (The state of New Zealand's environment 1997, 1997).

1.3 Native plant species: constructed wetlands and riparian margins

It has been found that uptake and accumulation of nutrients in plants is correlated with root length and root morphology; both are factors that define the plant’s ability to reach available nutrients (Hopkins & Huner, 2004; Tinker & Nye, 2000). An important distinction in root morphology, for example, is found between monocotyledonous and dicotyledonous, and herbaceous and woody plant root systems (Klepper, 1991, 1992, as cited in Tinker & Nye, 2000). The native New Zealand plant species selected for this study have not been studied in the context of nutrient acquisition, but variable root lengths and morphologies have been accurately described in a previous study by Landcare Research, which compared the root structures of 15 native plant species (Integrated catchment management. Trial 1 results; Integrated catchment management. Trial 2 results; Phillips, Marden, Ekanayake, & Watson, 2008)(Figure 1). Information regarding the root morphology of *K. ericoides* is not currently available. Of the 6 native plant species selected for this study, 3 are monocotyledonous, and the other 3 are dicotyledonous. These plants were also selected with preference to those with longer root lengths, and availability for study. NZ native plants have evolved in environments that are widely variable in certain nutrients and trace elements based on their parent material (Curtis & Childs). I would hypothesize that they may have distinct elemental profiles when compared inclusively as well as to pasture species, which are well studied.
Considerable amounts of information have also been published on the use of constructed wetlands for treatment of surface runoff from pasture lands both in New Zealand and internationally (Geary & Moore, 1999; Healy, Rodgers, & Mulqueen, 2006; Tanner, 1995; Tanner, Clayton, & Upsdell, 1995; Tanner, Nguyen, & Sukias, 2004). However, little information has been published regarding the implementation of planted riparian margins for the purpose of managing nutrient and contaminant fluxes from pasture lands and no information is known about the chemical properties of the selected New Zealand native plant species. Riparian planting has been implemented in New Zealand since European colonization for the management of stream bank stabilization, shelter belts and sources of timber. Traditional plantings however consisted mainly of exotic Salix sp. and Populus sp., probably due to their rapid growth rates and the aesthetic preferences of Europeans. The use of native plant species in riparian planting schemes is an emergent trend in New Zealand.

Figure 1 – Total structural root length (m) of 3 year old native plant species (Phillips et al., 2008). Species selected for this study are Kohuhu (Pittosporum tenuifolium), Karamu (Coprosma robusta), Cabbage Tree (Cordyline australis), Flax (Phormium tenax), Toetoe (Cortaderia richardii) and Kanuka (Kunzea ericoides) (not included in the graph).
A recent study has found that the use of native plant species as shelter belts on New Zealand dairy farms yielded higher species richness of native spiders and beetles than shelterbelts of exotic plants (Fukuda, Moller, & Burns, 2011). Additional study of the effect of riparian planting in New Zealand has reported a positive trend between water quality and on farm best management practices which included presence of riparian plantings and exclusion of cattle from riparian margins (Wilcock et al., 2009). In order to maximize the effectiveness of native riparian plantings, it is necessary to identify which plant species have the greatest potential to buffer surface and groundwater from sources of nutrient and contaminant flux.
1.4 Aims and objectives of the study

The aim of this study is to investigate the potential of selected NZ native species suited to riparian zones for the management of nutrient and contaminant fluxes on dairy farms.

Objectives

1. To elucidate the chemical composition of selected native plants and their accompanying rhizospheres with a view to their potential use to improve environmental outcomes in NZ farming systems.

2. To determine the effect of established NZ native plants in paddock margins on the composition components of dairy shed effluent following its application to soil.
2. Sites and Methods

2.1 Study Soils

The Canterbury Plains are the largest alluvial plains in New Zealand, covering 750,000 ha. The plains are a series of gently sloping fans established by the gravel outwash from four major rivers – the Waimakariri, Rakaia, Ashburton and Rangitata. Greywacke rocks have been eroded from the mountains following successive periods of glaciation have been washed out by the rivers and deposited to depths of 500 m. Overlying loess, a mixture of sand, silt and clay from the riverbeds has been deposited across the south-east alluvial fans by north-westerly winds (Molloy, 1998).

The study site for this experiment has a soil classification of Templeton silt loam. Templeton soils are regarded as being among the most fertile, agriculturally important soils in Canterbury (Table 1). Templeton soils cover approximately 75,000 ha (10%) of the intermediate terraces of the Canterbury lowlands. They consist of deep layers of silty/sandy alluvium that had been deposited 10,000 to 3,000 years ago. They have a much higher water-holding capacity than the associated shallow and stony Eyre and Lismore soils. These deep soils of the seasonally dry Canterbury Plains are important because of their greater ability to withstand drought, and to provide the most efficient use of water when irrigation is applied (Molloy, 1998).
Table 1. Soil chemical properties for the Templeton silt loam. Values in brackets represent the standard error of the mean (n=3 unless otherwise indicated) (Knowles, Robinson, Contangelo, & Clucas, 2011)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>K (mg/kg)</th>
<th>Na (mg/kg)</th>
<th>1401 (119)</th>
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<tbody>
<tr>
<td>pH</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC (cmol(+)/kg)</td>
<td>12.4 (0.5)</td>
<td>Na (mg/kg)</td>
<td>136 (4)</td>
<td></td>
</tr>
<tr>
<td>C%</td>
<td>2.0 (0.1)</td>
<td>Cd (mg/kg)</td>
<td>0.4 (0.1)</td>
<td></td>
</tr>
<tr>
<td>N%</td>
<td>0.18 (0.001)</td>
<td>Cr (mg/kg)</td>
<td>11.6 (0.4)</td>
<td></td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>518 (25)</td>
<td>Cu (mg/kg)</td>
<td>4.5 (0.1)</td>
<td></td>
</tr>
<tr>
<td>S (mg/kg)</td>
<td>193 (15)</td>
<td>Pb (mg/kg)</td>
<td>12.0 (0.1)</td>
<td></td>
</tr>
<tr>
<td>Ca (mg/kg)</td>
<td>3005 (101)</td>
<td>Zn (mg/kg)</td>
<td>43 (1)</td>
<td></td>
</tr>
<tr>
<td>Mg (mg/kg)</td>
<td>855 (11)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The Templeton soil at the site of the present study has supported an irrigated dairy farm since 2001 (SIDDC, 2010). Prior to this, the land supported a dry sheep pasture since the mid-19th century, which replaced a mosaic of wetland, forest and shrub habitats.

2.2 Study Plants

Six native species of plants were selected for use in this study, as described below. These species have a natural distribution in the area of the present study and were likely to have been present prior to the conversion to sheep farming in the mid-19th century.

*Phormium tenax* (Xanthorrhoeaceae) – Harakeke, Korari (the flowering stem), New Zealand Flax:

A tall, perennial, tufted plant with woody rhizomes from which long sword-shaped leaves are emitted in a fan shape. The leaves are exceedingly tough, hence the Latin name *tenax* meaning holding fast, in reference to the strong leaf fibres. The natural distribution of *P. tenax* is widespread throughout New Zealand. This particular species prefers damp soils (Eagle, 2006).

Plate 2. *Phormium tenax.*
**Cortaderia richardii (Poaceae) – Toetoe:**

There are five native species of *Cortaderia* in New Zealand collectively known as Toetoe, with an additional naturalized South American species known as pampas grass. *C. richardii* is a tall tussock with narrow, erect sharp leaves and narrow inflorescence. *C. richardii* is found throughout New Zealand’s south island on river beds, lake and stream margins and wet places and has been found to grow from sea level to 900m (Edgar & Connor, 2000).

**Pittosporum tenuifolium** (Pittosporaceae) - Kohuhu, Black Matipo, Rautawhiri:

A small, round headed tree 4-10 m in height with a slender trunk that reaches 40-50 cm in diameter. The bark is often dark to black in appearance with an almost blistered appearance. A pungent odor is released when the branches are broken. The natural distribution of kohuhu is coastal as well as hill country forests and shrublands, up to an altitude of 900 m. They can be found throughout the North Island and east of the main divide in the South Island. It is absent from the West Coast of the South Island as well as from Stewart Island (Wardle, 2011).
*Cordyline australis* (Asparagaceae) – Common Cabbage Tree, Ti Kouka:

The genus *Cordyline* includes about 15 species, six of which occur in New Zealand. Of these six, one was introduced by Maori (*C. terminalis* (=*fruticosa*)), one can be found also on Norfolk Island (*C. obtecta (= kasper*)), and the other four are endemic. Cabbage trees, together with nikau palms, are the only trees in New Zealand that fall into the plant class *Monocotyledones* (Wardle, 2011). The common cabbage tree is widespread throughout both main islands of New Zealand and can be found anywhere from eutrophic wetlands to coastal headlands and in mountainous regions up to 800 m in altitude (Wardle, 2011).

*Coprosma robusta* (Rubiaceae) – Karamu, Kakaramu

Karamu is a shrub or small tree which can grow to a height of up to 6 m. It has stout spreading branches with smooth bark that changes from green to a pale brown with maturity.

There are two species referred to as Karamu, *Coprosma robusta* and *C. lucida*, and are widespread across the North Island and occur in the South Island as far south as North Otago in the east and Greymouth in the west. *C. robusta* is prevalent from the coastal regions up to about 1200 m in altitude and from swamp-lands to cliffs and rocky outcrops (Wardle, 2011).
Kunzea ericoides (Myrtaceae)– Kanuka, White Tea-tree

Kanuka can reach heights of 20 m with a diameter at breast height (dbh) of up to 0.6 m. However, it is often found growing as a shrub or up to 15 m high and 35 cm in diameter. In open habitats, Kanuka branch profusely producing a bushy shrub or small rounded tree, whereas in dense stands the branches and foliage are often confined to just the upper canopy. The bark is a grey to light-brown, papery, and sheds from the trunk and branches in long strips.

The distribution of Kanuka ranges from the Three Kings Islands southwards, but is absent from Stewart Island and the Chatham Islands. It can be found from sea level to 1,000 m in altitude, but prefers the drier eastern side of the country (Wardle, 2011). This species probably formed the dominant scrub vegetation cover in undisturbed soil on the Canterbury Plain dryland (Fukuda et al., 2011).

Lolium perenne (Poaceae)– English or Perennial ryegrass:

A loosely to densely tufted perennial growing 10-90cm high. The culms are erect or spreading, slender with 2-4 nodes and smooth. The leaves are green and hairless with sheaths that are smooth. The basal area is usually pinkish when young. In the northern hemisphere, ryegrass flowers from May to August (Hubbard, 1954).
Considered to be the most important of all the cultivated fodder grasses, it the first grass to be cultivated in Europe and the first to be sown homogenously (Bews, 1929). *L. perenne* is now grown extensively in temperate countries throughout the world (Bews, 1929; Hubbard, 1954) and is widely planted in intensive dairy pastures with an average renewal rate of 6% per annum in New Zealand (Mercer, 2011).

2.3 Description of sampling area

The Lincoln University Commercial Dairy Farm was chosen as the location for this study as being close to campus, with management practices well recorded. The farm, which was converted from a dry sheep farm to an irrigated dairy farm in 2001, was planted with native plant species along riparian margins and areas beyond the center pivot irrigators in 2008 (Steed, 2009). These areas are delineated by electrical fencing to prohibit grazing from cattle. The selected sampling area was chosen for its accessibility and availability of desired plant species to be sampled. The location of this sampling area is along Ellesmere Junction Road in Springston, New Zealand. The planting area is triangular in shape and located at the south-western end of a cattle pasture. Drainage ditches run along two of the three sides of the sampling area, with cattle pasture adjacent to the third side (Figure 2). Although this site may not be considered a riparian area, information gained from this study may be utilized in riparian planting schemes. Access to the sampling site is gained via Ellesmere Junction Road.
In addition to the native plant sampling sites, treatments include a reference effluent application to non-vegetated soil, and a reference treatment of non-vegetated soil without the application of effluent (the latter to account for natural seasonal variations) (Chen, Condron, Davis, & Sherlock, 2003). Each treatment has five replicates randomly selected, with individual even-aged plants (of similar size within each species). Reference plots were selected within the same sampling area at locations that do not have any plants growing within at least 2 m. It was desired to have the reference plots within the sampling area to avoid differences in soil structure and hydrology. However, due to the density of the planting area, 2 m spacing was all that could be provided. It is recognized that a spacing of 2 m will not completely exclude the influence of adjacent plants on the reference plots.
2.4 Establishment of sampling sites

Wooden frames measuring 30 cm x 30 cm (inner surface area of 900 cm squared) and constructed from 3 x 10 cm untreated Monterey Pine (*Pinus radiata*) were placed against the plant stem and inserted into the soil to a depth of 2.5 cm to prevent surface runoff from the effluent application (Figure 3). This process was repeated for both the control and pasture trials. Adjacent to each wooden frame, and opposite of the selected plant, a hole of 50cm deep and 30cm square was dug using a conventional spade. The edge of each hole was kept 10 cm from the inner edge of the frame to prevent direct seepage of effluent into the sampling holes. Each sampling hole was covered by a piece of untreated plywood to prevent erosion, direct accumulation of rain or snow, or from any persons or animals from falling in. Each sampling site received a numbered tag for individual identification.

Figure 3– Diagram of established sampling site including the locations of the soil core samples, frame for effluent application, location of the sampling pit and locations of the rhizon samplers within the sampling pit.
2.5 Sampling Methods

The rhizon soil moisture samplers used in this study were obtained from Eijkelkamp Agrisearch Equipment (en.eijkelkamp.com/). These samplers have a body diameter of 2.5mm and a length of 10cm. They are constructed from a porous polymer material with a 0.1 micron pore size. The samplers are attached to a coextruded tubing (PE inside/ PVC outside) with a 1mm internal diameter and a luer connector for attaching to a vacuum tube or syringe. This sampling process does not affect the pH and provides for a filtered sample that can be analyzed directly. For the purpose of this study, the luer connectors have been fitted to needles for use with the 9mL vacuum tubes (Plate 9). Installation of the rhizon samplers included the use of a 2.35mm stainless steel rod, which was acquired from the Lincoln University Field Research Center. The rod was used to bore a horizontal pilot hole into the soil profile for ease of installation and to prevent breakage of rhizon samplers.

![Plate 9: Photograph of fully assembled rhizon sampler coupled with a syringe and vacuum tube.](image)

Prior to the installation of the rhizon samplers, a brief trial was used to evaluate the need for any equilibration of the rhizon samplers once installed into the soil profile. This was determined by fitting vacuum tubes to several samplers that had been installed in various sampling holes at depths of 15 and 30 cm. The vacuum tubes were monitored for signs of functional operation. Rhizon pore water samplers were then installed into the plants rhizosphere on 26/8/2011 at depths of 15 cm and 30 cm from the soil surface. Rhizon samplers used in the preliminary trial were removed, and all new samplers were installed to preserve uniformity among the Rhizon samplers. After an equilibration period of 6 days,
pore water samples were taken from each sampling site prior to the application of effluent to gain base-line data.

Vegetation and soil samples were taken from each of the sampling sites. The comparative analysis of these samples may show the potential abilities for each plant species to accumulate elements that are found in the soil. Vegetation samples were collected from 5 locations spanning the vertical length of the live canopy for *C. robusta*, *P. tenuifolium* and *K. ericoides*. The vegetation sample size from each sampling location was consistent within each species set, however due to the differences in leaf size between species the quantity of leaves sampled between species was not equivalent. For *P. tenax*, *C. fulvida* and *C. australis*, only one leaf was taken from the middle of the vertical length of the canopy due to the larger mass of the leaves from these species (Figure 4).

![Diagram showing areas of the plants sampled for chemical analysis.](image)

Soil and vegetation samples were taken from the opposite side of each plant from the frames and sampling holes to reduce any chance of disturbance during installation of the frames and sampling holes (Figure 3). Two soil samples were taken from each site using a 2 cm diameter soil corer to a depth of 10 cm. The samples were taken in a linear path from the sides of each frame, leaving a 30 cm distance between each soil sample location. For each reference site, a distance of 30 cm was used to simulate the presence of a plant stem for determining distance from the wooden frame. Pasture grass and soil samples were taken...
from patches growing within the sampling area as well as from the north-east adjacent paddock. Five of these samples were from various locations within the planted sampling area and five from various points within the paddock, taken no further than 50 meters from the fence line. To avoid collection of effluent with the soil and vegetation samples, soil samples were taken at approximately 50 cm distances and vegetation samples were taken from anywhere between those sets of soil samples. A soil analysis was performed to investigate differences in elemental concentrations between soil samples from the research plot to soils sampled from the paddock.

**Slurry Application**

Approximately 200 L of dairy cattle effluent was collected from the Lincoln University Commercial Dairy Farm. The effluent was collected by hand into 20 L plastic containers as it flowed into the storage pond from the milking platform (see illustration 9). It was then mixed together in a 200 L plastic drum to produce a homogenous solution. The collected effluent was chemically analyzed to identify the presence and concentrations of elements. The effluent samples analyzed were collected at the beginning, middle and end of the process of returning the effluent from the drum back to the containers to ensure adequate mixing. The effluent was then stored at 5°C in a refrigerator. The plastic containers were also used to facilitate transportation of the effluent to the sampling site.

Plate 10– Image of effluent pit and collection of effluent for slurry application. (Photograph by M. Simmler, personal communication, 2011)
A total of 35 locations received an application of effluent, applied within the area of each wooden frame. Slurry application rates were based on the effluent’s nitrogen concentration to reflect recommended realistic slurry application rates of 50 kg N ha$^{-1}$ for grazed pasture systems in Canterbury (Cameron, Di, Moir, Christie, & Pellow). The slurry contained 450 mg l$^{-1}$N, thus requiring exactly 1 L of slurry per 30 cm x 30 cm quadrat.

The five sampling sites without plants, acting as references to measure natural seasonal variations within the soil were also fitted with wooden frames, but did not receive an application of effluent. Instead, these seasonal variation controls have received an equal volume of tap water from Lincoln University.

Plate 11. Application of effluent slurry to sampling sites. (Photograph by N. Dickinson, personal communication, 2011)

Following the application of effluent, the initial two sets of samples (labeled Slurry 1 & Slurry 2) were collected as soon as they had accumulated enough water required for chemical analysis. This was done to provide more insight on the dispersion of the contaminants within the soil profile during the flush. Samples were then taken weekly, given that there was adequate precipitation. Samples were analyzed by the author and/or Lincoln University technicians. Sampling dates are listed in Table 2.
Table 2. Vacuum tube insertion and collection dates over the 12 week sampling period:

<table>
<thead>
<tr>
<th></th>
<th>Inserted</th>
<th>Collected</th>
<th>Collection period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline data</td>
<td>1-9-2011</td>
<td>6-9-2011</td>
<td>5 days</td>
</tr>
<tr>
<td>Slurry 1</td>
<td>4-10-2011</td>
<td>6-10-2011</td>
<td>2 days</td>
</tr>
<tr>
<td>Slurry 2</td>
<td>9-10-2011</td>
<td>14-10-2011</td>
<td>5 days</td>
</tr>
<tr>
<td>Slurry 3</td>
<td>14-10-2011</td>
<td>21-10-2011</td>
<td>7 days</td>
</tr>
<tr>
<td>Slurry 4</td>
<td>21-10-2011</td>
<td>28-10-2011</td>
<td>7 days</td>
</tr>
<tr>
<td>Slurry 5</td>
<td>28-10-2011</td>
<td>5-11-2011</td>
<td>8 days</td>
</tr>
</tbody>
</table>

Soil moisture and soil temperature data corresponding to the duration of the study was obtained from the NIWA National Climate Database. The data was collected by NIWA from their Broadfield climate station located approximately 3.5 km NW of the research plot.

Morphological characteristics and metabolic traits unique to each individual plant species may cause variances in the surrounding physical environment that are a reflection of those features. Soil moisture (%) will be recorded from 15cm and 30cm depth at each of the 80 soil leachate sampling sites.

2.6 Analytical Methods

All vegetation samples were rinsed with deionized water, the leaves were separated from the stems and the stems were discarded. All vegetation and soil samples were placed in labeled paper bags and dried at 105°C in an oven for 7 days. Following drying, vegetation samples were finely grounded with a Yellow-line A10 grinder. The soil samples were crushed with a mortar and pestle and sieved to 2mm. All samples were then sealed in plastic bags before being digested and analyzed.

ICP-OES

All vegetation samples and 10 soil samples (from 5 of the native plant species (P. tenax, C. richardii, P. tenuifolium, C. robusta and K. ericoides), and samples from each of the locations within the adjacent paddock (5 samples)) were analyzed with a Varian 720-ES.
Inductively Coupled Plasma Optical Emission Spectrophotometer fitted with an SPS-3 autosampler and ultrasonic nebuliser. Prior to ICP-OES analysis, the samples were processed in a CEM MARS Xpress microwave digester. For digestion, vegetation samples were weighed to 0.5g and transferred into digest tubes. Vegetation samples then received 8ml HNO₃. Soil samples were weighed to 0.5g and transferred into digest tubes. Soil samples then received 5ml HNO₃ and 1ml of H₂O₂. All samples were left overnight to predigest in a fume cupboard. During microwave digestion, samples were placed inside Teflon PFA and Kevlar shielded vessels and subjected to rapid heating (175°C) and elevated pressure (for 20 minutes), causing the samples to digest or dissolve. Digested samples were filtered through Whatman No. 52 filter paper into 25ml volumetric flasks. Digest tubes and remaining residue on the filter paper were rinsed several times with deionized water and diluted up to 25ml, then transferred to 30ml vials and refrigerated until analysis. Results from the ICP-OES analyses included concentrations for Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr, Tl, and Zn values in mg/kg. These results also included reference, certification and percent recovery values. All methods used were in accordance to Lincoln Universities Laboratory Users Guide by Cresswell & Hassall (n.d.).

Leachate samples from the primary, baseline data collection event were analyzed at Canterbury University with their Inductively Coupled Plasma Optical Emission Spectrophotometer (ICPOES). The leachate samples were measured out to 3ml and were acidified with 200μm of HNO₃. These samples included one blank consisting of 3ml deionized water acidified with 200μm HNO₃. Results from the ICPOES analysis of leachate samples included concentrations for Li, Be, B, C, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U.

**Total Carbon and Nitrogen**

Total carbon and total nitrogen was analyzed for all vegetation and soil samples using a LECO CNS-2000 Elemental Analyser. Samples were weighed out to 0.2g for ground vegetation and 0.5g for sieved soil. The samples were combusted at 1250-1450°C in an
oxygen atmosphere, converting any elemental carbon and nitrogen into CO$_2$, N$_2$ and NO$_x$.

Any NO$_x$ is then reduced to N$_2$ and all gasses are passed through infra-red cells to determine carbon content, and a thermal conductivity cell to determine N$_2$. Analysis included the use of control and repeated samples for quality assurance. All methods used were in accordance to Lincoln Universities Laboratory Users Guide by Cresswell & Hassall(n.d.).

**Ion Exchange Chromatography**

Ion analysis of all leachate samples was completed using a Dionex DX-120 Ion Exchange Chromatograph fitted with a Dionex AS50 Autosampler and intergrated by Chromeleon Peaknet 6.0. The system is also suppressed with an Anion Self-Regenerating Suppressor (ASRS-Ultra) and detection is by conductivity. Sample preparation consisted of diluting 200μl of leachate with 800μl of deionized water. Where samples would normally need to be filtered with a 0.2μm membrane prior to analysis, the samples were filtered to 0.1μm during collection by the rhizon soil moisture samplers. Results from the anion analysis included chloride, bromide, nitrate and sulphate concentration values. All methods used were in accordance to Lincoln Universities Laboratory Users Guide by Cresswell & Hassall(n.d.).

**Flow Injection Analyzer (FIA)**

Ammonia concentrations within the soil leachate samples was analyzed with a FS 3000 flow injection analyser. As the leachate samples were filtered to 0.1μm during collection by the rhizon soil moisture samplers, no other preparation was needed for this analysis.

**pH**

Soil samples were collected from each of the native plant species and reference sites, separate patches of ryegrass growing within the research plot and from various
locations within the dairy paddock adjacent to the research plot. It was desired to test the soils as well as the collected leachate samples for their pH as the pH of soil affects the mobility of elements and activity of microbes within the soil profile (figures 15 & 16). Analysis of the soil pH was determined by weighing 10g ± 0.05 air-dried soil into a 70ml vial followed by 25mls of deionised water. The samples were covered and shaken before being left overnight to stabilize. For both soil and soil leachate, the pH meter was calibrated using buffers of pH4 and pH7. The pH meter probe was rinsed with deionised water and dried between samples.

Statistical analysis

Statistical data analysis was completed with the use of Minitab 16. Data from ICP-OES soil and vegetation analysis results as well as anion analysis results of the baseline data was processed using a one-way Anova with the Fishers individual error rate. A P-value of 0.05 was used to determine significance amongst the data. Score plots were created to determine patterns amongst the data.
3. Results

3.1 Soil properties

Results of the soil analysis showed little difference in soil elemental composition beneath native plant species within the research plot (Table 3). However, analysis did present significantly (p < 0.05) greater concentrations of N(%), as well as Ca, Cd, P, and S (mg/kg) in the paddock soils when compared to the soils from within the research plot. A carbon/nitrogen ratio was included to determine the potential for N mobility. The dividing line between immobilization and release of N is about 20:1. Values greater than 30:1 results in immobilization, 20-30:1 results in neither immobilization or release of mineral N and ratios less than 20:1 enables a release of mineral N (McLaren & Cameron, 1996).

Table 3. Chemical properties of the soils. Values in brackets represent the standard deviation of the mean. For Research Plot Soil pH, C% and N%: n=6. Otherwise n=5 (Research Plot Soil pH, C% and N% have been calculated from mean values of all 6 native species); For Paddock Soil: n=5; For soluble elements: n=10 (soluble data was calculated from the reference sites of the research plot); Units of mg/kg are not associated with pH, C% and N%; (*) = significant differences (P<0.05) in concentrations between Research Plot Soil and Paddock Soil; (n.d.) = no data. Note that there were no significant differences between species within the research plot.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Paddock Soil (mg/kg)</th>
<th>Research Plot Soil (mg/kg)</th>
<th>Soluble at 15cm (mg/l)</th>
<th>Soluble at 30cm (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.25</td>
<td>4.71</td>
<td>5.93</td>
<td>5.65</td>
</tr>
<tr>
<td>C%</td>
<td>3.70 (0.47)</td>
<td>3.16 (0.10)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>N%</td>
<td>0.36 (0.05) *</td>
<td>0.31 (0.01) *</td>
<td>57.6 (36.23)(NO₃⁻)</td>
<td>72.5 (37.09)(NO₃⁻)</td>
</tr>
<tr>
<td>P</td>
<td>1178 (173.7) *</td>
<td>961 (67.3) *</td>
<td>0.12 (0.04)</td>
<td>0.03 (0.01)</td>
</tr>
<tr>
<td>C:N ratio</td>
<td>10.3</td>
<td>10.2</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Al</td>
<td>23463 (897)</td>
<td>23418 (797)</td>
<td>0.22 (0.04)</td>
<td>0.09 (0.02)</td>
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<td>-----</td>
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<td>As</td>
<td>6.85</td>
<td>8.12</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>(0.45)</td>
<td>(0.47)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>(0.004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br^-</td>
<td>n.d.</td>
<td>n.d.</td>
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<td></td>
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<tr>
<td></td>
<td>0.93</td>
<td>(0.21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>5270</td>
<td>4437</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(154) *</td>
<td>(356) *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>43.6</td>
<td>(7.60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.65</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.03) *</td>
<td>(0.04) *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02E-2</td>
<td>(0.03E-3)</td>
<td></td>
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<tr>
<td>Cl^-</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
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<tr>
<td></td>
<td>17.9</td>
<td>(8.42)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>23.9</td>
<td>23.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.00)</td>
<td>(0.83)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06E-2</td>
<td>(0.04E-3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>8.57</td>
<td>7.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.53)</td>
<td>(0.29)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.05E-1</td>
<td>(0.05E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>19659</td>
<td>19802</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(708)</td>
<td>(331)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>(0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>3846</td>
<td>3942</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(162)</td>
<td>(202)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.09</td>
<td>(2.10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>37.45</td>
<td>37.11</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>(1.14)</td>
<td>(0.43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03E-1</td>
<td>(0.08E-2)</td>
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<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1642</td>
<td>1657</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(18.20)</td>
<td>(10.96)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.22</td>
<td>(1.68)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>624</td>
<td>548</td>
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<td></td>
<td>(25.77)</td>
<td>(36.82)</td>
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<tr>
<td></td>
<td>0.04</td>
<td>(0.02)</td>
<td></td>
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<tr>
<td>Na</td>
<td>271</td>
<td>278</td>
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<tr>
<td></td>
<td>(18.97)</td>
<td>(13.13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.69</td>
<td>(1.13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>12.03</td>
<td>11.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.37)</td>
<td>(0.13)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03E-1</td>
<td>(0.03E-2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>21.38</td>
<td>22.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.72)</td>
<td>(0.66)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02E-2</td>
<td>(0.07E-3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>426</td>
<td>377</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(31.97) *</td>
<td>(31.43) *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.93 (6.21) (SO_4^{2-})(mg/l)</td>
<td>14.72 (6.50) (SO_4^{2-})(mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>86.02</td>
<td>85.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.73)</td>
<td>(1.45)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>(0.16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>(0.22)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2 pH analysis of soil and leachate samples

Soil pH greatly affects numerous soil chemical reactions and processes and has often been referred to as the master variable of soils (Sparks, 2003). Soil pH within the paddock was significantly (P<0.05) higher than that of all other soil samples (Figure 5). Soil leachate pH gradually increased with depth on all samples taken except for those taken at the reference sites treated with H2O, which decreased with depth (Figure 6).

Figure 5. Soil sample pH (n=10 for the reference, for all others n=5)

Figure 6. Mean soil leachate pH from 15cm and 30cm depth (n=5)
3.3 Chemistry of the plant rhizospheres

Data collected from the rhizospheres of the selected native plants provides insight into their phytoremediation capabilities including the potential for accumulation and phytostabilization. Although some significant differences were found, the biological significance of these findings is questionable (except for NO$_3^-$ under *C. richardii*). Elemental concentrations of soil leachate samples from beneath the plants was compared to leachate samples taken from the reference sites for significant differences (p < 0.05). Table 4 presents the findings from the baseline data collection event prior to the effluent application.

Table 4. Significant differences in the native plant rhizosphere leachate chemistry in comparison to reference sites. Non-significant differences are not shown. (< reflects values less than the reference; > reflects values greater than the reference. For reference sites n=10. For plant species n=5.)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Species</th>
<th>Value @ 15cm depth</th>
<th>Value @ 30cm depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>Reference</td>
<td>57.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>202.42 (&gt;</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Reference</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td><em>P. tenax</em></td>
<td>0.04 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>0.03 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. australis</em></td>
<td>0.04 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>P. tenuifolium</em></td>
<td>0.04 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. robusta</em></td>
<td></td>
<td>0.04 (&lt;)</td>
</tr>
<tr>
<td>Si</td>
<td>Reference</td>
<td>5.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>3.38 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. robusta</em></td>
<td></td>
<td>7.31 (&gt;</td>
</tr>
<tr>
<td>Cl</td>
<td>Reference</td>
<td>10.06</td>
<td>10.68</td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>20.53 (&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>P. tenuifolium</em></td>
<td>18.36 (&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>K. ericoides</em></td>
<td>17.87 (&gt;</td>
<td>21.78 (&gt;</td>
</tr>
<tr>
<td>Fe</td>
<td>Reference</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>0.01 (&lt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. australis</em></td>
<td>0.01 (&lt;)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Reference</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>C. robusta</em></td>
<td></td>
<td>0.005 (&gt;</td>
</tr>
<tr>
<td>Sb</td>
<td>Reference</td>
<td>0.0028</td>
<td>0.0026</td>
</tr>
<tr>
<td></td>
<td><em>C. richardii</em></td>
<td>0.0037 (&gt;</td>
<td>0.0034 (&gt;</td>
</tr>
<tr>
<td></td>
<td><em>C. australis</em></td>
<td>0.0037 (&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>P. tenuifolium</em></td>
<td>0.0038 (&gt;</td>
<td>0.0032 (&gt;</td>
</tr>
<tr>
<td></td>
<td><em>C. robusta</em></td>
<td></td>
<td>0.0034 (&gt;</td>
</tr>
<tr>
<td></td>
<td><em>K. ericoides</em></td>
<td></td>
<td>0.0035 (&gt;</td>
</tr>
</tbody>
</table>
3.4 Effect of effluent application

Analysis of soil leachate samples from 15cm depth has identified *C. richardii* as having a significantly (*p* < 0.05) greater concentration of nitrate (NO$_3$) when compared to other native plant species (Figure 7).

![Graph showing nitrate concentrations in leachate samples from 15cm depth.](image)

*Figure 7. Nitrate concentrations in leachate samples from 15cm depth.*
3.5 Soil moisture and soil temperature during leaching experiment

Changes in soil moisture may affect the concentrations of elements within the soil leachate through dilution. The increase in soil moisture recorded from 04/10/11 – 06/10/11 reflects a decrease in elemental concentrations observed for samples collected during this timeframe. An inverse trend between soil moisture content and elemental concentration was consistent for all anion samples analyzed within the leachate solution.

Tinker & Nye (2000) report that low temperatures may affect the uptake rate of certain elements within the rhizosphere. Soil temperature has been recorded to allow for comparisons between trends amongst the data. It is uncertain as to whether soil temperature was low enough to affect the plants abilities of elemental uptake. Soil moisture and soil temperature data corresponding to the duration of the study was obtained from the NIWA National Climate Database (Figure 8).

![Figure 8. Mean soil moisture and soil temperature during sampling events. Data obtained from NIWA database.](image)
Morphological characteristics and metabolic traits unique to each individual plant species may cause variances in the surrounding physical environment that are a reflection of those features. Soil moisture (%) was recorded from 15cm (Figure 9) and 30cm (Figure 10) depth at each of the 80 soil leachate sampling sites on July 14th 2012. The Broadfields NIWA Climate Database reported a soil moisture % of 33.6 at 20cm depth during this time.

Figure 9. Soil moisture % at 15 cm depth beneath sample sites. Means that do not share a letter are significantly different.

Figure 10. Soil moisture % at 30cm depth beneath sample sites. Means that do not share a letter are significantly different.
3.6 Elemental concentrations in plants

Data collected from the analysis of elemental concentrations in plant foliage samples provides insight into the phytoremediation capabilities and potential abilities for selected plant species to accumulate particular elements. Figure 11 presents the significant differences (p < 0.05) of mean elemental concentrations in plant foliage between species. Means that do not share a letter are significantly different in elemental concentration and their potential abilities to accumulate each respective element.
Figure 11. Elements with significant differences in concentration between species as found in vegetation samples (concentrations are that of dry matter). Means that do not share a letter are significantly different.
3.7 Groupings of plants according to their aboveground chemistry

It was desired to elucidate the chemical composition of selected native plant species. A score plot was created from results of the vegetation analysis to investigate the possibility of similarities and differences in the chemical composition between plant species. Components used for this analysis included Ca, Cu, Fe, K, Mg, Mn, P, S, Zn and total N. Elements selected for the score plot analysis were selected based on a combination of available data and the essentialness of these nutrients for plant health. The results of this analysis formed three distinct clusters segregating ryegrass from native monocots from native dicots. Apparent similarities between morphological characteristics and differences between species based on chemical composition are presented in Figure 12.

![Score Plot of Ca, ..., N](image)

Figure 12. Score plot depicting differences following ICP-OES analysis from plant foliage samples
Table 5. Eigenvalues for score plot (see figure 22)

<table>
<thead>
<tr>
<th></th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
<th>PC5</th>
<th>PC6</th>
<th>PC7</th>
<th>PC8</th>
<th>PC9</th>
<th>PC10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eigenvalue</td>
<td>4.84</td>
<td>2.58</td>
<td>0.85</td>
<td>0.52</td>
<td>0.35</td>
<td>0.30</td>
<td>0.24</td>
<td>0.15</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>Proportion</td>
<td>0.48</td>
<td>0.26</td>
<td>0.09</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cumulative</td>
<td>0.48</td>
<td>0.74</td>
<td>0.83</td>
<td>0.88</td>
<td>0.91</td>
<td>0.94</td>
<td>0.97</td>
<td>0.98</td>
<td>0.99</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 6. Principal Component Analysis for score plot (see figure 22). These components account for 74% of the variation.

<table>
<thead>
<tr>
<th>Principal Component Analysis:</th>
<th>PC1</th>
<th>PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-0.17</td>
<td>-0.38</td>
</tr>
<tr>
<td>Cu</td>
<td>0.41</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe</td>
<td>0.38</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>0.41</td>
<td>0.07</td>
</tr>
<tr>
<td>Mg</td>
<td>0.18</td>
<td>-0.48</td>
</tr>
<tr>
<td>Mn</td>
<td>-0.03</td>
<td>-0.54</td>
</tr>
<tr>
<td>P</td>
<td>0.42</td>
<td>-0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.38</td>
<td>-0.05</td>
</tr>
<tr>
<td>Zn</td>
<td>0.11</td>
<td>-0.57</td>
</tr>
<tr>
<td>N</td>
<td>0.36</td>
<td>0.03</td>
</tr>
</tbody>
</table>
4. Discussion

4.1 Soil chemistry

There was a clear distinction in soil fertility between the sampling site and the adjacent dairy paddock. Dairy pasture management for 11 years has significantly elevated soil pH, N, P, Ca, S and Cd through inputs including effluent irrigation, fertilizer application, liming, urine patches and cattle feces. Soils within the research plot have a pH below the optimum for pasture production. The lower soil pH within the research plot may have attributed to fewer significant differences between the soil leachate samples by making certain elements less available (N, P, K, S, Mo, Ca, Mg, Mo and B). Likewise, other elements may have been more available due to the lower pH (Fe, Mn, Zn, Cu and Co) (Figure 13).

![Figure 13. Effect of pH on microorganisms and the availability of nutrients important in plant growth. As the band for a particular microbe or nutrient widens, the activity of the microbe or availability of the nutrient becomes greater (Brady, 1984 as cited in Sparks, 2003).](image)

When compared to the nutrient rich, highly managed soils in which *L. perenne* is cultivated, New Zealand native plant species may be better adapted to the nutrient
deficient environments with generally more acidic soils in which they have evolved. In this regard, the soils in the research plot may be more representative of a typical natural New Zealand environment than that of a dairy farm. Therefore, New Zealand plants may be more efficient at acquiring some of these nutrients that occur at low concentrations in the soil due to their natural adaptations. If an area of dairy farm were retired from agricultural usage and planted with native species, it would not likely receive the same high nutrient inputs as the rest of the farm and would probably eventually return to a lower state of fertility. Nutrient runoff from the farm may still provide higher than natural nutrient levels. It is unclear if this has occurred on our study plot. A possible exception to this situation may potentially include fertilizer application onto a dedicated area planted with valuable native plant species. An example of this may be that of Kanuka (*Kunzea ericoides*) or Manuka (*Leptospermum scoparium*) for the purpose of high quality honey production. The present study shows that *K. ericoides* appears to effectively manage N, P, Zn, Cu and Mn in less fertile low pH soil. It is difficult to predict how these native plants may perform in a high nutrient environment, and there is no known evidence in the literature.

### 4.2 Foliage chemistry

There was a distinction between monocots and dicots in regards to elemental accumulation in the foliage samples (Figure 21 & Table 7) with monocots accumulating more Mo, Cr, Na and Ni; and dicots accumulating more Ca, Cu, Mg, Mn, P, S, Zn, N(%), B, Cd, Al and Sr. In terms of overall elemental uptake patterns, multivariate analysis of these data (Figure 22 and Tables 5&6) revealed clear distinctions between pasture grass and native species. PC1 explained 48% of variation, weighted heavily on N, P, K, S and Cu. These elements, with the exception of S, are all phloem mobile in plants. Native species divided clearly into monocots and dicots along PC2 (26% of variation), these also being separated from the ryegrass. PC2 was heavily weighted on phloem-immobile elements (Zn, Mn, Ca, Mg and B).

According to Suttle (2010), plants may react to inadequate supplies of available elements in the soil by limiting their growth, reducing the concentration of the deficient elements in their tissues or, more commonly, by reducing growth and concentration
simultaneously. The extent to which a particular response occurs varies with different minerals and different plant species or varieties and with the soil and climatic conditions. In addition to natural factors (e.g. season, climate) and man-made (e.g. provision of irrigation, fertilizer, shelter) changes in elemental composition occur throughout plant maturity (Suttle, 2010).

The specific patterns of elemental uptake by the selected plants may reflect the environments in which the plants have evolved. For example, after reviewing the significant differences of elemental concentrations in the plant foliage (Figure 21), L. perenne had a greater quantity of elements that were of significantly higher concentration when compared to the native plant species, reflecting its demand for nutrients.

4.3 Solutes and slurry application

There were few differences in soluble leachates in the soil, either between plant species or with reference unplanted plots. The exception to this was nitrate which was significantly higher under C. richardii. This corresponded to lower levels of soil moisture beneath these plants, and may therefore be a result of a concentration effect. Differences in soil moisture between plant species may occur beneath the plants as variations in plant morphology affect the degree of interception during precipitation. This change in water flux would influence soil moisture levels and may affect the concentrations of elements within the soil leachate samples. However, it would also have been expected that this would influence P. tenax, which has a similar morphology, or plants with dense canopies such as P. tenuifolium. Another possibility is that the rhizosphere of C. richardii is suitable to host greater quantities of nitrifying bacteria compared to other selected plant species and reference sites. These potential higher rates of nitrification could be tested by the addition of a known concentration of NH$_4^+$ to the rhizospheres. NH$_4^+$ concentrations collected within the soil pore leachate from the effluent application were below detection limit. For the purposes of this study, 50 kg N/ha$^{-1}$ was used to determine the volume of effluent applied to each sampling site. However, urine patches can contain localized concentrations of 500-1000 kg N ha$^{-1}$ (McLaren & Cameron, 1996, p. 271). Increasing the volume of effluent applied to the soil surface may have resulted in an increased effect on concentrations of elements
measured within the soil pore water. However, when planted within an enclosed riparian margin, native plants would not likely be subjected to these higher concentrations, and results would therefore not be reflective of practical conditions.

The accumulation of elements into the plants biomass is not essential in the process of phytoremediation. According to Kruger et al. (1997), plants impact contaminant reduction principally by providing an optimal environment for microbial proliferation in the root zone, which often leads to enhanced degradation of chemicals in vegetated compared to non-vegetated soils. The presence of vegetation in soils also creates a convection of solutes within the soil solution towards the plants roots due to evapotranspiration. This mass flow may sufficiently influence soil hydraulics to prevent further attenuation of contaminants (Dickinson, Baker, Doronila, Laidlaw, & Reeves, 2009). Table 4 illustrates elemental concentrations within the soil leachate of the selected plants that are of significant difference compared to samples taken from the reference sites (B, Cl, Cu, Fe, Sb and Si). These differences may indicate either accumulation or stabilization of these elements by the selected plants.

The effluent application trial provided unanticipated results with lower than expected concentrations of elements measured in the pore water. Numerous environmental parameters including but not limited to soil temperature, soil moisture, soil oxygen concentration, $\text{NH}_4^+$ availability, and pH value have been shown to act as important physiological constraints and therefore influence nitrification rates in terrestrial ecosystems (Roberson and Tiedje, 1987; Booth et al., 2005; Cookson et al, 2006; Silva et al., 2005 as cited in Stange & Neue, 2009). Monitoring and data collection of environmental parameters did not include soil oxygen concentration, or $\text{NH}_4^+$ availability from the applied effluent. Tinker & Nye (2000) report that low temperatures may affect the uptake rate of certain elements within the rhizosphere. However, soil temperature at 20cm depth increased from 6 - 12.5 °C within the 11 week sampling period during which time soil moisture was relatively high. No significant effect on leachate concentrations were observed during this time. As the soils within the research plot are substantially more acidic than soils within the adjacent paddock, there may have been less of an effect of rhizosphere acidification, resulting in fewer differences in soil leachate composition than may have occurred within soils with a higher pH.
Among the confounding variables, it is recognized that preferential flow could have potentially had an impact on the results of the effluent treatment. Earthworms and other soil organisms can create channels in soil which can allow rapid water flow under saturated conditions. Similarly, plant roots may provide pathways through the soil which increase the hydraulic conductivity (McLaren & Cameron, 1996). Earthworm activity, root growth, freezing and thawing, wetting and drying cycles and natural disturbances such as earthquake cracks can lead to the development of surface-connected macropores in the soil. Water flow through these macropores can have two distinct effects on leaching. The first is when solutes are present in the infiltrating water, or when water is applied immediately after a solute, and then macropore flow will lead to extensive leaching at faster rates than normal. The second effect occurs when solutes are present within aggregate micropores then they may be bypassed by the bulk of the flowing water and thus protected from leaching (McLaren & Cameron, 1996). Some of the effluent may have drained through macropores, resulting in the low concentration levels in the leachate samples. Leaching via macropore flow was not quantified within the results of this study. However, the fact that we did not detect a significant difference between the unplanted reference sites indicates that this may not be the reason.

4.4 Management of nutrient and contaminant flux

Comparative analysis of the chemical composition of soil samples found significant differences in concentrations of N, P, S, Cd and Ca between the soils from the research plot and the soils sampled from the adjacent paddock. Elevated concentrations of N, P, S and Cd are likely to be a result of management practices including fertilizer application. These elements could potentially leach from paddock soils into surface and groundwater, resulting in environmental and human health concerns and should be managed where possible. An evaluation of vegetation and soil leachate results revealed potential abilities for the remediation of N, P, S and Cd through the use of selected plant species. Potential means of contaminant remediation through the use of native plant species investigated in this study include:
Nitrogen

Nitrogen has been clearly identified as a source of eutrophication of surface waters (Carpenter et al., 1998; Smolders, Lucassen, Bobbink, Roelofs, & Lamers, 2009). Contamination from excessive N is often a result of applications of inorganic fertilizers, dairy effluent, animal manure, biosolids, as well as septic systems, and municipal sewage systems (Sparks, 2003). Exposure to excessive N, in the form of nitrates, has been linked to methemoglobinemia, or blue baby syndrome, abortions in women (Centers for Disease Control and Prevention, 1996 as cited in Sparks, 2003) and increased risk of non-Hodgkins lymphoma (Ward et al., 1996).

Due to its negative charge, nitrate ($\text{NO}_3^-$) is repelled by cation exchange sites and is therefore readily leached when water drains through the soil (McLaren & Cameron, 1996). Loss of nitrate is generally greatest during late autumn, winter and early spring when plant uptake of nitrogen is low, there is an excess of rainfall and the soil is at or near field capacity. Regardless of the source of nitrate, if concentrations are greater than plants can readily assimilate then leaching will occur when water drains through the soil (McLaren & Cameron, 1996). Nitrate is more likely to leach through sandy soil than clay soil, even under the same climatic conditions (McLaren & Cameron, 1996; Sparks, 2003). Considerable amounts of nitrogen leach from intensively grazed pastures within New Zealand, sometimes as much as 200 kg N ha$^{-1}$ yr$^{-1}$.

Nitrogen levels found within the foliage samples of $K$. ericoides were comparable to levels found within the ryegrass samples taken from within the paddock. These concentrations were significantly greater than those of the other native plant species. As ryegrass is known for its high demand for nitrogen, it is thought that the relative concentrations of N may mean that $K$. ericoides also shares a high demand for and ability to accumulate N.

Soil leachate analysis revealed significantly higher concentrations of nitrate at 15cm depth beneath $C$. richardii when compared to all other leachate samples taken. These findings may be attributed to greater levels of nitrifying bacteria and/or greater capabilities to phytostabilize nitrate when compared to other native plant species. However, these
findings may also be attributed to dryer soil conditions beneath *C. richardii* when compared to soil moisture beneath other native plants.

The ranked numerical order of N concentrations by species is not consistent between nitrate in leachate samples and N in vegetation samples. If higher nitrate levels in the leachate samples of *C. richardii* is attributed to greater levels of bacteria, then the plant species potential ability to perform nitrification is not equivalent to its ability to accumulate N when compared to the other selected species. Results from a soil leachate analysis of ammonia were mostly below detection limit and did not provide enough data to provide any additional insight.

**Phosphorus**

Phosphorus has been identified as a major contributor to surface water eutrophication (Carpenter et al., 1998; Smolders et al., 2009; Stutter, Demars, & Langan, 2010). Contamination from excessive P is often a result of applications of inorganic fertilizers, dairy effluent, animal manure, biosolids, as well as septic systems, and municipal sewage systems (Sparks, 2003). As a result of both electrostatic and non-electrostatic bonds to soil particles, P is generally not a concern to groundwater contamination. However, P contamination of surface water readily results from surface runoff and erosion of particulates (Sparks, 2003). In New Zealand, dairy farm management practices involve regular reseeding of paddocks. This process involves eradicating the current crop by spraying the paddock with glyphosate, followed by direct drilling of new grass and clover seed (Thom & Glassey, n.d). These actions leave paddocks susceptible to wind and water erosion and greater quantities of surface runoff, which may transport contaminants such as P to surface water. Nguyen and Sukias (2002) identified drainage ditches within pastoral catchments as a potential means of P transport to receiving waters with significant amounts of P in both surface and subsurface sediment.

Of the native plant species studied, *K. ericoides* had a significantly greater concentration of P within the foliage when compared to other native plant species. Soil leachate analysis did not present any conclusive evidence for phosphate. This was potentially due to the set detection limit of the chromatograph. (This was necessary to be able to facilitate the higher concentrations of the other elements analyzed.)
concentrations in the soil leachate samples may have also been below detection limits due to the general immobility of phosphate through the soil profile. Greater quantities of phosphate may have been detectable if soil leachate was sampled closer to the soil surface.

**Sulfur**

Sulfur has been found to indirectly lead to eutrophication of surface waters. Smolders et al. (2009) found that under certain soil conditions, increased phosphorus availability coupled with wide spread nitrate leaching from agricultural lands can indirectly provoke strong internal phosphate eutrophication in wetlands through interference with sulfur and iron biogeochemistry in the subsoil. Nitrate is able to mobilize sulfate from geological pyrite deposits through the oxidation of FeSx in the aquifer, leading to a decrease of nitrate and an increase of groundwater sulfate concentrations. The increase in sulfate concentrations may provoke strong phosphate eutrophication in wetlands fed directly or indirectly (via surface water) with groundwater as sulfate strongly interferes with iron phosphorus chemistry and stimulates anaerobic decomposition of organic matter.

Vegetation analysis has identified *C. robusta* as having comparable concentrations of S in the vegetation samples compared to that of *L. perenne* grown in the same soil. *C. robusta* has also been found to have significantly greater concentrations of S within the vegetation samples than that of other native species, with the exception of *C. richardii*.

**Cadmium**

Considered to be one of the most ecotoxic metals, cadmium exhibits adverse effects on all biological processes including those of humans and animals, as well as plants. Although the mobility and plant availability of Cd may be limited in wetland soils, it has been found to be readily available to plants in upland soils (Grambrell 1994 as cited in Kabata-Pendias & Mukherjee, 2007). This metal has the potential to adversely affect the environment, and it may also degrade the quality of food resources. Cd input to soils in New Zealand from P-fertilizer has been cited at 8.9g ha⁻¹ yr⁻¹ whereas the average value of Cd input to EU countries is at 2.5g ha⁻¹ yr⁻¹ (Kabata-Pendias & Mukherjee, 2007). Cadmium has the ability to replace zinc biochemically, causing high blood pressure and kidney damage, destroy testicular tissue and red blood cells, and is toxic to aquatic biota (Sparks, 2003). The
input of fertilizers to New Zealand agricultural soils has caused a double increase of Cd concentrations compared to their non-agricultural soils (N. F. Suttle, 2010).

Vegetation analysis revealed significant differences between plant species with *P. tenuifolium* and *C. robusta* having the greatest concentrations of Cd within the foliage samples. Both *P. tenuifolium* and *C. robusta* on average had greater concentrations of Cd within the foliage samples than that of the soil within the research plot. *P. tenuifolium* had a 10 fold greater concentration of Cd in its foliage compared to foliage of *L. perenne* and exceeded concentrations found within the paddock soils.

4.5 Riparian planting scheme for paddock margins

Figure 14 depicts a plan for riparian planting based on the findings of this study. This plan has been based on findings presented in Table 7. It is desired to establish a planting that is self-sustainable with weed control and regeneration. *C. richardii* has been planted directly up to the fence edge in order to prevent the invasion of ryegrass from the paddock. Without being subjected to grazing, *L. perenne* will seed and spread throughout the riparian planting, resulting in competition of seed germination from native plant species.

Figure 14. Recommended riparian planting plan for paddock margins based on study results.
K. ericoïdes has been found to have similar concentrations of N(%) in the vegetation samples as the L. perenne samples from the paddock. If a riparian buffer strip was planted with C. richardii and K. ericoïdes, then the potential ability of C. richardii to convert ammonium into nitrate could be used to supply K. ericoïdes with plant available N for attenuation and remediation. Species C. robusta and P. tenuifolium have been included within this plan as vegetation analysis has revealed that these species exhibit a greater potential of elemental uptake than any other native species investigated in this study.

Although it is not a native plant species, L. perenne was found to have accumulated significant quantities of various elements compared to native plant species selected for this study. However, a difference between L. perenne and the native plant species is that the root morphology of L. perenne is shorter in length than that of the other native plant species, and a plants ability to absorb nutrients is limited by its ability to reach them. Therefore, it may be limited in use for riparian buffer plantings, but may still provide beneficial services by filtering surface runoff or shallow lateral contaminant flux prior to the riparian margin.

Carex secta, a plant species that was not included in this study has been incorporated into the riparian plan along the water’s edge. Although the remediation properties of this plant have not yet been explored, the root morphology (Figure 1) and additional characteristics including tolerance for saturation and extended hydro-periods are likely to benefit stream-bank stabilization and filtering of suspended solids from surface runoff. Carex secta has been omitted from this study as it is only found at the lowest regions of the riparian zone at the location of our sampling area and a seasonally high water table prohibits the use of the methods selected for this study in this location.
Table 7. Presentation of findings by species: identifying native plant species ideal for riparian and paddock-edge planting (X = concentrations of greatest significance; + = concentrations less than those marked with ‘X’, but still significantly greater than all others; * = concentrations were not significantly greater than that of *Lolium perenne* (ryegrass) samples)

<table>
<thead>
<tr>
<th>Element</th>
<th><em>C. australis</em></th>
<th><em>P. tenax</em></th>
<th><em>C. richardii</em></th>
<th><em>K. ericoides</em></th>
<th><em>P. tenuifolium</em></th>
<th><em>C. robusta</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>N (%)</td>
<td></td>
<td></td>
<td>X (in leachate)</td>
<td>X*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X*</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td>+*</td>
<td></td>
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</tr>
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<td>Ca</td>
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<td>Zn</td>
<td></td>
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<td>+*</td>
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<td></td>
<td>X</td>
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</table>

4.6 Use as fodder for nutritional supplements

Livestock obtain nutrients from the feeds and forages they consume, and nutrient intake is influenced by the factors that determine the elemental composition of the plants and their parts. Elemental concentrations in plants are largely dependent on four factors including: plant genotype, soil environment, climate and their stage of maturity (Suttle, 2010). The importance of each factor for determining elemental accumulation in plant species varies between elements. Additionally, aspects of pasture husbandry including the use of fertilizers, soil amendments, irrigation, reseeding, intercropping and use of high yielding cultivars may further influence elemental accumulation between plant species (Suttle, 2010). These factors may also influence nutrient and contaminant fluxes from dairy paddocks.
Elemental concentrations found in the selected native plant species are likely to reflect factors inflicted upon the study location. Elemental concentrations in plants generally reflect the adequacy with which the soil can supply absorbable elements to the roots (Suttle, 2010). It is expected that these values would change if the selected species were located on a retired section of dairy paddock and subjected to other variables such as amended soil, nutrient flux, higher pH (Figure 23) and irrigation. Given the many factors that can influence a plants nutritional value, it is difficult to compare the values and limitations of the plant species selected for this study to traditional crop or forage species which are cultivated in fertilized and pH amended soils. Likewise, the potential use of identifying species for buffering nutrient and contaminant fluxes from the environment may also be subject to change.

According to The Nutrient Requirements of Dairy Cattle (Nutrition, Nutrition, & Council, 2001), trace mineral deficiencies of dairy cattle often include Co, Cu, I, Mn, Se and Zn. Some of these elements were found at significant levels in the foliage of the plants selected for this study. Copper concentrations were greatest in L. perenne, however concentrations from selected native plants showed no significant differences in copper concentration. Manganese concentrations were significantly greater in P. tenuifolium and K. ericoides when compared to all other plants. Zinc concentrations were significantly greater in P. tenuifolium and K. ericoides when compared to other plants.

According to The Nutrient Requirements of Dairy Cattle (Nutrition et al., 2001), elements that may cause impairment to animal wellbeing or product quality include Cd, F, Pb and Hg. Cadmium concentrations were significantly greater in P. tenuifolium and C. robusta when compared to all other plants and may potentially be detrimental if browsed upon.
5. Conclusions

Significant differences in pH and elemental composition were found between the soils retired from agriculture and the adjacent paddock soils which are intensively managed. Variations in soil temperature had little apparent effect on rhizosphere chemistry over the early spring months. A contrasting trend developed between soil moisture levels and elemental concentrations within the soil leachate samples. Significantly higher concentrations of nitrate were found within the soil leachate beneath *C. richardii*. However, differences found in soil leachate chemistry may be influenced by differences in plant physiology and root morphology. New Zealand native plant species are found to have distinct patterns of elemental accumulation when comparing native monocots and dicots as well as to exotic ryegrass. Foliage concentrations of N, P, K and S were highest in ryegrass (*L. perenne*), although significant differences between native plant species were found. Foliage concentrations of Cd were up to 10 fold higher in native plant species when compared to ryegrass. Some native plants exhibit elemental properties that could potentially be suitable as fodder supplements. However, these findings are reflective of the environmental conditions in which these plants have been grown.

Overall, the results of this study indicate that planting native species on productive agricultural land in New Zealand offers potential advantages in terms of nutrient and trace element management. This could be of benefit to both agriculture and environment. There is sufficient evidence to show that soil conditions differ beneath native species of plants and with soil planted with shallow-rooted pasture grass. It is a reasonable assumption that this is likely to modify lateral and vertical fluxes of nutrient-enriched drainage water in riparian zones. Trace element uptake differs significantly between native plant species to the extent that selective planting on paddock borders may also add value through avoidance of deficiency diseases in stock. These potentially useful findings justify further research.
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Appendix I

Overview of relevant phytoremediation science

“Phytoremediation is a technology that uses various plants to extract, contain, immobilize or degrade contaminants from soil and water for the purpose of the remediation of these contaminants from the environment” (Saleh, Huang, Greenberg, & Glick, 2004). The processes of phytoremediation include all plant-influenced biological, chemical, and physical processes that aid in the accumulation, sequestration, degradation, and metabolism of contaminants, either by the plants or by the free-living organisms that constitute a plant’s rhizosphere (Cunningham et al., 1995, 1996; Macek et al., 2000 as cited in Saleh et al., 2004, p. 115). In comparison to other remediation engineering techniques, phytoremediation is a rather new technology and has been found to be effective at addressing a wide variety of surficial contaminants. Some target applications for phytoremediation include contamination from metals, metalloids, petroleum, hydrocarbons, pesticides, explosives, chlorinated solvents, and industrial byproducts (Cunningham, Shann, Crowley, & Anderson, 1997).

Phytoremediation is most applicable to sites where the pollutants are of low to moderate concentration, close to the soil surface, relatively non-leachable, cover large surface areas and where conventional remediation technologies would be prohibitively expensive (Saleh et al., 2004; Singh & Ward, 2004). Cunningham et al. (1997) state that “the primary market driver for continued research in this area is the significant cost reduction these systems appear to afford”. In 1997, total costs of non-plant based remediation (calculated on a m³ basis, in US dollars) range from $10 to $100 for in-situ remediation, $30 to $300 for ex-situ processes and can easily surpass $1,000/m³ for specialized in-situ techniques such as vitrification. Yet phytoremediation can cost as low as $0.05/m³ (Cunningham et al., 1997). The use of phytoremediation technology includes additional secondary advantages to more intensive remediation technologies. Contaminated lands that
are designated for phytoremediation can also provide environmental benefits including provision of habitat, aesthetic qualities, as well as social, recreational and cultural benefits.

There are however inherent limitations to phytoremediation in that plants are living organisms with specific oxygen, water, nutrient and pH limits that must be maintained (Cunningham et al., 1997). Other limitations include that of the depth of contamination, concentration of the contaminants and the given time frame for project completion. Although for the most part current practices of phytoremediation are technically sound, they are far from optimized and biological resources for phytoremediation remains largely untapped (Cunningham et al., 1997).
Appendix II

Overview of relevant soil science

Soil particle size distribution is separated into 3 main classes including sand, silt and clay. The clay particles are the smallest of the three and give the soil many of its key chemical and physical properties with its ability to adsorb and hold nutrients as well as water. Sand and silt particles provide less in the form of nutrient supply or storage, unless they are coated with clay (McLaren & Cameron, 1996, p. 60). Soils possess the ability to adsorb and hold contaminants as well as nutrients. Unlike water and air in which contaminants are readily diluted and dissipated, soil is a more static media where contaminants with low mobility (e.g. metals and lipophilic compounds) may be present for much longer periods of time. Contaminated soils may show little inherent improvement over many decades and can continue to further affect groundwater, neighboring areas, and bodies of surface water (Cunningham et al., 1997).

There are several transport mechanisms for contaminants within the saturated and unsaturated zones. However, these mechanisms are dependent upon soil properties including texture, porosity, specific yield, permeability and attenuation capacity (Holzmann, 2010). Within the unsaturated zone, contaminants are filtered as they flow down through the soil. This process, called soil attenuation holds the contaminants allowing for microbial processing or phytoremediation (Holzmann, 2010).

If the soils are coarse, thin, have high permeability or are subjected to inundation of groundwater then the chances of contaminants reaching the groundwater increases (Holzmann, 2010). When this occurs, a plume forms from the source of groundwater entry. The formation of the plume is referred to as dispersion and can occur both mechanically and molecularly. Mechanical dispersion only happens when there is a flow within the groundwater whereas molecular dispersion can occur under either flowing or stagnant conditions (Holzmann, 2010). The level of contaminant concentration is highest at the source of entry to the groundwater and the concentration decreases as the contaminants
move in the direction of the groundwater flow. The rate of contaminant transport is dependent upon the rate of flow of the groundwater and is known as advection and the decrease in concentration is referred to as diffusion and happens by dilution from an addition of water (Holzmann, 2010). Convection encompasses and is the sum of both the advection and diffusion transport processes. Depending on the amounts of clay minerals or organic matter within the aquifer, some contaminants may be removed from solution by a process known as adsorption. Contaminants may also return to the unsaturated zone through a process known as volatilization whereby the dissolved contaminants change from the aqueous phase to a vapor phase and travel up through a capillary fringe (Holzmann, 2010).
Appendix III

Additional implications of implementing riparian plantings

Anthropogenic implications

A critical attribute revealed by this study is that implementation of these results can lead toward the improvement of human health through improved drinking and swimming water quality conditions. Numerous health problems in New Zealand have been traced to high levels of nitrate in the groundwater including blue baby syndrome, a blood disease in infants (Ministry for the Environment, 2010). By filtering out excess nutrients, riparian plants may prevent the invasive growth of aquatic plants that under eutrophic conditions blanket swimming holes. Some riparian plants may also prevent bacteria and pathogens from entering surface water.

Beyond health benefits, riparian plantings have an increasing aesthetic value to New Zealanders. The desire for increasing the quantity of native plants is particularly strong in Canterbury where less than 1% of the native vegetation remains and most of the region has been classified as acutely threatened (Environment Canterbury Regional Council, 2011). These figures place Canterbury as one of the lowest regions in New Zealand for native vegetation.

Riparian plantings act similar to hedgerows, blocking both the wind as well as providing visual impedance of the agricultural landscape beyond. Being similar to hedgerows, taller riparian plantings can also reduce drift of effluent during irrigation/fertilization events occurring in high winds.

An additional benefit of implementing the results of this study is that of a recreational value. By minimizing the runoff of nutrients into the waterway, providing shade over the water and increasing the vegetation within the littoral zone, increased habitat for recreationally harvestable species such as whitebait and trout may result.
Increasing habitat also provides additional opportunities for bird watching or hunting of waterfowl.

Although these benefits may be expected from most riparian planting schemes, application of the most effective plant species and habitat structures would enhance the effectiveness of the riparian planting.

Environmental implications

Riparian buffer zones provide many important functions including but not limited to filtering of polluted overland and subsurface flows from nearby agricultural areas, influencing the type and amount of terrestrial carbon inputs to streams, control over the duration and magnitude of flood events, protecting banks of water bodies against erosion, filtering polluted air, reducing intensive growth of aquatic macrophytes through shading, improving microclimates, creating new habitats and ecotones, and creating more connectivity in landscapes due to habitat corridors and stepping stones (Collier et al., 1995; Leecce et al., 2006; Mander et al., 2005; MfE, 1997; Vigiak et al., 2010).

Perhaps one of the most important environmental implications of riparian plantings is the provision of habitat corridors. These corridors act as a means of achieving connectivity, facilitating species or populations of plants or animals to move amongst landscape elements in a mosaic of habitat types between two or more patches of otherwise disjunct habitat (Hilty, Lidicker & Merenlender, 2006; Lidicker, 1999; Taylor, Fahrig, Henein & Merriam, 1993; Tischendorf & Fagrig, 2000 as cited in Garven, 2012). Functioning as habitat corridors, riparian plantings may promote beneficial services including exchanges in genetic material, ecosystem functions and food web dynamics (McCoy, 2009 as cited in Garven, 2012). A landscape void of habitat corridors may result in a decrease in species richness (Spellerberg, 1993 as cited in Garven, 2012) which may consequently lead towards homozygosity, genetic drift, inbreeding and a decreased ability for adaptation (Dawson, 1994 as cited in Garven, 2012). Further consequences may result in depletion of genetic variance of an area and eventually result in species extinction. An important distinction should be made however that the quality of riparian plantings is indeed reflective of its functionality as a working system. For example, a study by Fukuda et al. (2011) noted that
use of native plant species as shelter belts on New Zealand dairy farms yielded higher species richness of native spiders and beetles than shelterbelts of exotic plants.
Appendix IV

Additional information regarding selected plant species

*Phormium tenax*- Leaves are 1-3 m long, 5-12 cm broad and can be keeled, stiff, erect or curving towards the tip with a leathery feel. The leaves are glaucous beneath with margins and midrib orange or red, the butt is heavy and often brightly colored (Eagle, 2006).

Flowering generally occurs in November and are dull red on their abaxial surface. The flowers are produced from a 5m tall erect panicle, are hermaphrodite, nectiferous and the perianth is tube shaped with 6 segments, 3 inner and 3 outer with 6 stamens. Seed capsules are roughly 8 cm long, dark brown to blackish, upright, thick and persistent, splitting in three when ripe. Seeds are black, glossy, flat and very numerous (Eagle, 2006).

*Cortaderia richardii*- The leaf blades can develop to 2m x 2.5cm, are stiff with abundant minute prickle-teeth throughout. Culms grow to 2.5m with glabrous internodes (Edgar & Connor, 2000).

Inflorescence develop to 1m, are plumose, stiff, erect to pennant-shaped and drooping. Natural populations generally comprise 62% hermaphrodite and 38% female individuals; populations exclusively hermaphrodite were found in Mackenzie Country (Edgar & Connor, 2000).

*Pittosporum tenuifolium*- In juvenile specimens, the leaves are usually covered with a sparse mat of fine hairs that become smooth and shiny at maturity. The leaves are arranged in an alternate pattern on the branchlets and suspended on leaf stalks 1-2 cm long. The leaf blades are variable in size, usually 2.5-4 cm long by 1-2.5 cm wide, but can reach 7 cm in length. The leaves are slightly leathery in texture, shiny green to greyish-green above but paler beneath with margins which are usually wavy (Wardle, 2011).

Flowering occurs between September and November and are very dark purple but become almost black as they age. The flowers measure approximately 1 cm in diameter.
when fully open. The flowers contain nectar and give off an exquisite honey-like scent which becomes most intense on mild damp evenings and is apparent some distance from the tree. The scent attracts moths and other night flying insects, which probably aid pollination (Wardle, 2011).

_Cordyline australis_- The common cabbage tree will normally grow to a height of 8-12 m with a diameter up to 80-100 cm. However, these trees have been reported to grow to heights of 18 m and diameters of 3 m. As a cabbage tree develops following germination, it can initially appear as a small cluster of grass. During this time, the tree begins to develop a thick stem which grows downward to act as a taproot for stability. The tree progresses to form leaves that are flat, sword shaped and light green in color. They extend in length and thickness to become 40-100 cm long by 3-6 cm wide. These leaves often adhere to the trunk, covering its rough bark and straight, narrow and un-branched trunk with minimal taper and a diameter of 5-10 cm. At this point, the cabbage tree is 1-3 m in height and develops its first cluster of flowers. At this and subsequent flowerings, the stem forks with one or more branches until a compact round-headed tree is formed (Wardle, 2011).

Flowering occurs from October to December. However, this is variable with heavy flowering occurring on an average of about three year intervals, which is said to herald a hot dry summer. The flowers are creamy-white, bell shaped, 6-8 mm in diameter and are produced in large terminal erect or drooping clusters. These flower clusters may measure 60-120 cm in length by 30-60 cm wide with hundreds of flowers on each branch. The flowers contain both male and female parts, with no separation into petals and sepals (Wardle, 2011).

_Coprosma robusta_- The leaves are in pairs on opposite sides of the stems, are dark green on the upper surface and have a paler undersurface. With more or less wavy edges, the leaves may also be finely and minutely toothed. The midribs of the leaves sometimes extend beyond the leaf margin as a short sharp tip, and tapers gradually at the base to a rather stout leaf stalk. The leaf blade ranges in size from 7-12 cm in length to 3-5 cm in width with a stalk of 1-2 centimeters long (Wardle, 2011).

The flowers of the Karamu appear from September to November and occur in dense clusters on much divided flower stalks which arise from the leaf axils. The females produce
fruit that varies in color from orange to dark orange-red and sometimes yellow. The fruit measure 7-10 mm in length by 4-5 mm in width (Wardle, 2011).

*Kunzea ericoides* - The leaves are lance shaped and rarely exceed 1.2 cm in length by 3 mm in width. They are arranged either singly or in clusters of three to five along the fine branchlets. The leaves are soft to the touch and produce an aromatic smell when bruised that resembles eucalypt oil (Wardle, 2011).

Kanuka flowers early in its development, producing small white flowers 3-6 mm in diameter. Flowering occurs during the summer and in a profuse manner. The flowers occur either singularly or in clusters of up to five individuals (Wardle, 2011).
Appendix V

Draft manuscript for publication

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THE PHYTOREMEDIATION POTENTIAL OF NATIVE PLANTS ON NEW ZEALAND DAIRY FARMS

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Ecological restoration of marginal land and riparian zones in agricultural landscapes in New Zealand enhances the provision of above-ground ecosystem services. We investigated whether native endemic plant assemblages have remediation potential, through modifying soil nutrient and trace element mobility. Analysis of native plant foliage in situ indicated that selective uptake of a range of commonly deficient trace elements including Zn, B, Cu, Mn and Co could provide a browse crop to avoid deficiencies of these elements in livestock, although some native plants may enhance the risk of Mo and Cd toxicity. Native plant rhizospheres were found to modify soil physico-chemistry and are likely to influence lateral and vertical fluxes of chemical elements in drainage waters. Native plants on marginal land in agricultural landscapes could add value to dairy production systems whilst helping to resolve topical environmental issues.

KEY WORDS: trace elements, endemic plants, phytoremediation, restoration

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INTRODUCTION

As a result of some 80 million years and at least 2,000 km of evolutionary and geographic isolation, more than 80% of the native flora and fauna of New Zealand is endemic and found nowhere else. In a global context, human colonisation of these remote lands by both Polynesians (from about 700 years ago) and Europeans (about 200 years ago) was relatively recent and had profound ecological impacts, as is particularly evident in modern production landscapes. Dairy products are New Zealand’s biggest export commodity and conversion of agricultural land to intensive dairy farming is currently prevalent on the Canterbury Plain of South Island. This region has been described as the most modified and biologically depauperate lowland environment in the country (Winterbourne et al. 2008). All of the plants used in agricultural and forestry, and most plants in shelterbelts, hedgerows, parks and gardens are introduced species (Meurk 2008).

There is increasing interest in planting a diverse array of native trees and shrubs particularly in urban areas and on the margins of paddocks, farms and water bodies (Meurk & Swaffield, 2000; Muerk & Hall, 2006). European gorse, willows, poplars, and macrocarpa in hedgerows are being substantially replaced with native New Zealand plants. Besides the aesthetic and conservation benefits of restoring indigenous plant species to this landscape, increased provision of a range of ecosystem services is becoming clear; for example, hedgerows containing native plant species may provide improved conditions for crop pollination and disease and pest control (Sandhu et al. 2008). The potential role of riparian zones in removing nitrogen from vertical and lateral fluxes of water is well documented (Verhoeven et al. 2006; Hefting et al. 2006) although there appears to be limited supportive factual evidence (Correll 2005; Hill 1996). In particular, there is a paucity of information on the efficacy of different plant species. This paper investigates whether planting native species alongside the edges of dairy paddocks and water races is an opportunity to improve nutrient and trace element management in farming systems in New Zealand.

In dairy pastures there is a complex but well studied relationship between nutrient cycling, grazing effects and plant and soil properties (McDowell and Smith 2012; Mikola et al. 2009). Widespread geographical deficiencies of a number of trace elements (Cu, Co, Zn, Mg, Se, I) in plants
and animals in New Zealand are well defined; 20-30% of farms are deficient and fertilisers and supplements are routinely provided for both crops and stock. Contamination with non-essential trace elements, especially Cd from phosphate fertilisers (Rothbaum et al. 1986) and As from historical sheep-dipping sites (Sarkar et al. 2007) may be benign but are also frequently contaminative and harmful in an environmental context.

Uptake of nutrients and trace elements from the soil is species dependent (Magesan et al. 2012), but there is little knowledge of how this varies in New Zealand’s native plants. Palatability of native species has received some attention in the context of cellulose and phenolic content (Bee et al. 2011) and it has been found that the most palatable native species of trees have the potential to grow fast and may be in a relatively strong position to recover after grazing (Bee et al. 2007). There is known to be a wide variation in foliar chemical element concentrations among native species (Lambert et al. 1989), and that those with low foliar nutrient concentrations produce more phenolics (including tannins) (Wright et al. 2010). However, there has been little exploitation of knowledge from traditional Māori native fodder and food crops, even though some exotic species including willows have been studied in this context (Marmiroli et al. 2012).

Any excessive build up of chemical elements in soils and leakage to water courses may have severe environmental implications (Beare et al., 2010; Wilcock et al., 2009). With intensification of dairy production, it is now realised that elevated soil macronutrient concentrations in shallow-rooted ryegrass/clover dairy pastures require careful management (Wilcock et al. 2009). Modern spray irrigation systems are providing much improved water use efficiency whilst improved fencing of stock is now compulsory; the latter typically consisting of wire fencing and bordering woody vegetation. Nevertheless, intensification of farming and conversion to dairy farms continues to contribute a significant increase in the nutrient loadings of New Zealand’s lakes and rivers (Monaghan et al. 2007a; Wilcock et al. 2007).

The aim of this work was to determine whether there is significant variability associated with native plants foliage and rhizospheres that may be of benefit to agricultural production systems in Canterbury. We have targeted the early spring period that is typified by high soil moisture, substantially raised soil temperatures and early seasonal plant growth.
SITE AND METHODS

The study site was on a Templeton silt loam which is one of the most fertile, agriculturally-important soils covering 10% of the intermediate terraces of the Canterbury lowlands (Molloy 1998). An area planted with native species, five years before the present study, was located at the south-western corner of a dairy paddock (Figure 1). Drainage ditches run along two of the three sides of the sampling area, although these remain largely dry during the extended summer period (approximately November – April). Five replicate even-aged plants were selected of six of these species at separate locations, semi-randomly distributed within the plot (Table 1); reference plots were selected within the same sampling area at locations with no plants within at least 2 m. Glyphosate weed control had maintained a largely bare ground surface between plantings.

Foliar samples were collected from multiple parts of the canopy of each of the six plant species at the 5 locations. Soil and vegetation samples were taken from the opposite side of each plant from the frames using a 2 cm diameter corer to a depth of 10 cm. Pasture grass and soils were sampled from patches growing within the plot and from 5 locations in the adjacent dairy paddock.

Wooden frames (30 cm x 30 cm) were placed as close as practicable against the stems of each of selected plants, and inserted into the soil to a depth of 2.5 cm (Figure 2). Adjacent to each wooden frame, and opposite of the selected plant, a 30 cm x 30 cm pit (50cm depth) was dug, 10 cm from the inner edge of the frame. Rhizon soil moisture samplers (en.eijkelkamp.com/). 10 cm x 0.25 cm (0.1 micron pore size) were inserted at 15cm and 30 cm depth. After an equilibration period of 6 days, pore water was sampled. Dairy effluent was collected from the storage pond from the milking platform, and applied within each of wooden frame (total 35 locations). Slurry application rates were based on the effluents nitrogen concentration to reflect recommended realistic slurry application rates of 50 kg N ha⁻¹ for grazed pasture systems in Canterbury (Di and Cameron 2000; Monaghan et al. 2007b). The slurry contained 450 mg N l⁻¹, thus requiring 1 L of slurry per 30 cm x 30 cm quadrat. The five sampling sites without plants, acting as references to measure natural seasonal variations within the soil were also fitted with wooden frames, but received an equal volume of water in place of effluent. Leachate samples were then taken from the rhizon samplers after an equilibration period of 6
days and on 5 subsequent occasions over 11 weeks. Soil moisture and soil temperature data corresponding to the duration of the study was obtained from the NIWA Broadfield Climate Station located approximately 3.5 km NW of the research plot. Soil moisture was recorded (15cm and 30cm depth) using a moisture probe at each of the 80 soil leachate sampling sites.

Foliage samples were rinsed with deionized water, separated from stems, then dried (105°C), ground and sieved to 2mm. Vegetation and soil samples were microwave digested in 5M HNO₃ (+H₂O₂ for soil samples) then analysed using ICP-OES following standard methods. Total C and N were analysed using a LECO CNS-2000 Elemental Analyser. After 4x dilution, ion analysis of leachate samples was carried out using a Dionex DX-120 Ion Exchange Chromatograph, suppressed with an Anion Self-Regenerating Suppressor, with detection by conductivity. Ammonia concentrations within the soil leachate samples were analysed using a FS 3000 flow injection analyser. Reference soil and plant material (ISE-921 and IPE-100) was analysed for QA, achieving 91—108% of certified values.

RESULTS AND DISCUSSION

Macronutrient and trace element concentration in plants

Foliar concentrations of N, P, K, S were higher in ryegrass than native plants (Figure 3) and ryegrass generally had higher concentrations in the paddock than when it was growing in the native species plot. Significant differences also existed between the native species, with at least two-fold differences in N,P, K and S and a 10-fold difference in Ca. Biomass production is far higher in ryegrass, at about 10-11 t ha⁻¹ in this region, and overall uptake would be much higher than by native plants, which are generally slow growing and obviously have less value as stock fodder. With less grazing pressure, however, a large proportion of nutrients in native plant foliage does become incorporated into biomass or returned to soil through leaf fall.
Foliar trace element concentrations (Figure 4) were substantially more variable between species and, in contrast to macronutrients, were often higher in native species than in ryegrass. *Pittosporum tenuifolium* and *Coprosma robusta* often had highest concentrations of both macronutrients and trace elements; these two species took up tenfold more B than did ryegrass. Boron is known to improve fecundity in sheep and cattle (Suttle 2010), and these could be useful supplementary food plants for stock to graze on paddock edges. Manganese and Mo concentrations were high in *Pittosporum*, both are essential elements, involved in N metabolism and cycling. Whilst there was double the concentration of Zn in *Pittosporum* than in pasture grass, this species also accumulated seven-fold more potentially toxic Cd. However, elevated soil Cd is result of its residual co-occurrence in phosphate fertilisers and there would normally be less outside the farm paddocks.

Zinc deficiency in many New Zealand soils is associated with facial eczema in sheep and cattle, and with cystitis in horses, and is commonly provided a trace element delivered to stock through water trough supplements. Potentially, selective planting of *Pittosporum* around paddock margins and occasional nibbling of its foliage may negate this requirement.

High molybdenum was recorded in flax (*Phormium*); although this element catalyses certain enzymatic reactions and plays an important role in the nitrogen cycle herbage contents approaching toxicity for domestic ruminants (which are particularly sensitive to this element) are not unknown. In the diet of cattle, Cu:Mo ratios of <2:1 are toxic and dietary Mo of >10 mg kg\(^{-1}\) can cause toxicity regardless of copper intake (Picco *et al.* 2012); as little as 1 mg kg\(^{-1}\) may be hazardous if copper content is <5 mg kg\(^{-1}\) (dry-weight basis). Integrating New Zealand Flax into Land Management Systems has received some attention and flax leaves can be used to to weaner cattle through winter (McGrddy 2006) but this may not be wise on NZ soils, many of which are Cu deficient. On the other hand, the occasional browsing of NZ flax presumably results in Mo-rich faeces which may be a source of bioavailable Mo to leguminous species in the pasture.

There is much current interest in establishing kanuka (*Kunzea ericoides*), a very similar species to manuka (*Leptospermum scoparium*), both of which are valuable crops for high-quality honey production. Although kanuka is better suited to lowland Canterbury environments, they are both dominant early-successional woody shrubs over much of the New Zealand lowlands; the present
study shows they appear to be effectively manage N, P, Zn, Cu and Mn acquisition from the soil. Foliar Mn concentrations, another essential minor nutrient for plants and animals, were extremely variable between plant species, and highest in Kunzea, Pittosporum and Coprosma. There is a strong relationship between Mn and Co in soil; in well-developed New Zealand soils, Mn influences cobalt availability and subsequent uptake by plants (Zheng 2000). Cobalt deficiency is frequent New Zealand soils and B12 is absorbed from cobalt when it is consumed. There are varying degrees of cobalt deficiency throughout New Zealand and these generally require some additional supplementation in cattle and sheep.

In terms of overall patterns of elemental uptake, multivariate analysis of these data (Figure 5) revealed clear distinctions between pasture grass (both plot and paddock) and native species. PC1 explained 48% of variation, weighted heavily on N, P, K, S and Cu. These elements, with the exception of S, are all phloem mobile in plants. Native species divided clearly into monocots and dicots along PC2 (26% of variation), these also being separated from the ryegrass. PC2 was heavily weighted on phloem-immobile elements (Zn, Mn, Ca, Mg and B).

**Soil chemistry and native plant rhizospheres**

There was a clear distinction in soil fertility between the sampling site in the fenced-off corner of the paddock and the dairy paddock (Table 2). Dairy pasture management for several years at this site has significantly elevated soil pH, N, P, Ca, S and Cd, although there were no other obvious trace element deficiencies or excesses of metal(oids). Upper nitrate values of about 20 mg l⁻¹ are normally expected from soil extractions (Stewart, 1989), although peak winter concentrations > 40 mg l⁻¹ are recorded on winter-grazed forage crops on free-draining New Zealand soils (Smith et al. 2012). This indicates that background soluble nitrogen as NO₃⁻ in the plots of the present study was relatively high, representing 1.9-2.4% of total soil N. Both soluble N and Zn were recorded at highest concentrations at 30 cm depth in the research plot. Clearly, liming and fertilisation in the paddock were most likely to be responsible, although native plants themselves may be a small contributory
factor to lower pH (Figure 6). Some pore water acidification was evident in the lower layer of the rhizospheres of native plants.

Root systems of native plants suited to riparian zones have distinctly differing morphologies, in terms of rooting depth and root structure, ranging from the fibrous root system of *Cortadaria* tussock, through more substantial root systems of *Pittosporum* and *Coprosma* to deep, stout roots of flax and the substantial descending underground stems and long cord-like roots of cabbage trees. This introduces considerable variability into soil profiles through which water percolates, both laterally and vertically. In terms of influencing soil processes, organic exudates from plant root systems introduce substantial soluble carbon to the soil which modifies soil physico-chemistry and directly determines the abundance and functionality of both soil fauna and microbes (Esperschuetz et al. 2009; Bardgett and Wardle 2010; Wall et al. 2012). It would seem likely that the singular process of lowered soil pH in native plant rhizospheres, as found in the present study, may influence the solubility and mobility of key chemical elements.

There were few differences in soluble leachates in the soil, either between plant species or with reference unplanted plots (Table 3). Exceptions were nitrate and chloride which were significantly higher under *Cortadaria* than in reference soil without plant cover or beneath other plant species. This corresponded to drier soil beneath this large tussock grass (Figure 7), and is therefore likely to simply be a resultant concentration effect (rather than due to increased nitrification). Higher Cl⁻ in the rhizosphere of *Pittosporum* (lemonwood) and *Kunzea* (Kanuka) may have a similar explanation.

**Slurry application**

Leachate NO₃⁻ and NH₄⁺ at 15 and 30 cm were not significantly elevated above baseline concentrations following slurry application to the soil surface, beneath any plants or even in the case of where slurry was applied to the bare soil surface. There were no differences in NH₄⁺, NO₂⁻, Cl⁻, Br⁻ or S0₄²⁻, and PO₄³⁻ was below detection limits [data are not shown for non-significant variables]. Soil
beneath *Cortadaria* presented the only situation where NO$_3$ was significantly elevated in leachate samples (Figure 8), whilst NO$_3$ beneath *Coprosma* was significantly lower than other treatments. This was apparently unrelated to slurry application however. Soil temperature at 20cm depth increased from 6 - 12.5 °C over the 11 week sampling period during which time soil moisture was relatively high (Figure 9). Clearly this had no significant effect on leachate concentrations of these elements.

Little difference in soluble elements in pore water may have been due to high spring rainfall raising soil moisture, or of course may reflect a limitation of our study. Despite the targeting of sampling over the early summer period of high soil moisture and increasing soil temperatures, this may not have been optimal. Higher nitrate recorded under the tussock grass *Cortadaria* was unlikely to be due to increased nitrification since Cl$^{-1}$ was similarly high, but more likely due to less water flow beneath this species. Thus, an important difference between varying plant morphologies may be related to above-ground canopy interception of rainfall or its effect on infiltration of rainfall into the soil. Preliminary work applying dairy slurry to soil did not raise soluble N concentration in pore water over the subsequent 11 week sampling period, with no evidence of nitrification producing NO$_3$. It is possible that acidification in the surface layers of native plant rhizosphere may be related to the release of H$^+$ from nitrification processes. Work is continuing to establish the fate of this applied N but, at this stage we are unable to comment on whether the explanation for low pore water mobility is rapid binding and immobilization of organic N in soil, volatilization of NH$_3$ or denitrification through N$_2$O release. It is known that NH$_3$ emissions from land-spread slurries can account for more than 40% of Total Ammoniacal N (Nyord *et al.* 2012). Lesser amounts of N$_2$O production have been found previously to progressively increase over a 10 week period following slurry application, accounting for 2 to 10% of applied N (Oenema *et al.* 2007; R.R. *et al.* 2002). Our own data suggest that time of year of is a critical factor in terms of its influence of soil moisture and rhizosphere dynamics, and subsequent impacts on chemical speciation and mobility. This requires further attention.

Highly variable rooting profiles of New Zealand native plants have been previously described (Marden *et al.* 2005) [also see www.landcareresearch.co.nz]. Most of the species in the present study are recognised as riverbank protection plants and have extensive root systems that have considerable
potential to modify soil physico-chemistry. For example 38% of the biomass of *Cordyline australis* (cabbage tree) is below-ground, with a root spread of 3 m to depths of 1.75–2.00 m after 25 years (Czernin and Phillips 2005). *Phormium tenax* has a similarly extensive adventitious root system with particularly stout fleshy roots (Wehi and Clarkson 2007) that are likely to alter patterns of vertical water flow through soil. Both rooting systems differ substantially from the rhizomes and fibrous rooting mass of the tussock grass *Cortedaria richardii* which has an overall substantially longer total root length (Phillips et al, 2008). Clearly the rhizospheres of native species will have differential effects on the ingress, flow and discharge of water, and also on the speciation and mobility of chemical constituents of the soil.

**CONCLUSION**

The foliage of native plants contained highly variable concentrations of nutrients and trace elements and there is an opportunity to provide species for occasional grazing on paddock margins that may address trace element deficiencies in stock and remove the need for supplements. *Coprosma robusta* contained high foliar concentration of B and *Kunzea ericoides* contained high Zn, Cu and Mn. *Pittosporum tenuifolium* contained high B, Mn, Mo and Zn, although its high uptake of Cd where this is elevated in soils may make this an unwise choice due to potentially toxicity. High concentration of Mo in *Phormium tenax* is potentially useful, but may create toxicity issues if flax is planted on Cu-deficient soils. Differences in uptake of chemical elements between species were clearly related to the mode of transport within the plant, in terms of whether there is significant phloem mobility.

Without agricultural inputs and with the influence of deeper and more extensive rhizospheres of native plants, soil physico-chemistry on the margins of paddocks and adjacent to water courses differs substantially to managed pasture. Differences, for example in terms of soil pH, NO₃⁻ and mobile Zn, were also evident in deeper layers of the rooting profiles of native plants. However, the most significant influence on nutrient and trace element profiles appeared to be associated with the morphology of different species of plants, their interception or deflection of rainfall and the resultant
wetness of underlying soil. Selective planting of the large native tussock grass, *Cortadaria richardii*, may be particularly useful for intercepting lateral flow of nutrient-enriched drainage waters. A tussock-forming sedge, *Carex secta*, that thrives alongside waterways in Canterbury deserved further attention in this context.

Plant roots modify soil physico-chemistry, in turn regulating aboveground productivity, biodiversity and other essential life processes including storage and filtration of water (Bezemer *et al.* 2010; McNeill and Winwiarter 2004). Dependent on widely different morphologies of plant root systems (Marden *et al.* 2005; Dickinson *et al.* 2009; Robinson *et al.* 2009), the rhizosphere is likely to substantially modify the ingress and discharge of water and dissolved substances. There is a generally held belief that riparian planting helps to protect water bodies from polluted run-off and drainage effluents. However, in the present study, slurry application beneath the canopy of native plants did not lead to increased fluxes of nutrient or trace elements through the soil profile; in the case of nitrogen, this was probably due to some combination of immobilization, volatilization, denitrification or lack of nitrification. Further investigation, perhaps with higher application rates, may be worthwhile; an equivalent amount of 1200 kg N ha$^{-1}$ is typical of dairy farm urine patches (Di and Cameron 2000; Moir *et al.* 2012) to understand the mobility of chemical elements in native plant rhizospheres; potential benefits have not been proven in the present study. Streamside riparian vegetation is known to influence the health of waterways and how they function, but influences and explanations are complex involving a range of factors from the benefits of shading, livestock exclusion and upstream landscape management. Over the last 10 to 15 years, there has been a surge in stream-restoration projects in Canterbury by a range of agencies, community groups, and rural landowners (www.niwa.co.nz).

Overall, the results of this study indicate that planting native species on productive agricultural land in New Zealand offers potential advantages in terms of nutrient and trace element management. This could be of benefit to both agriculture and environment. There is sufficient evidence to show that soil conditions differ beneath native species of plants and with soil planted with shallow-rooted pasture grass. It is a reasonable assumption that this is likely to modify lateral and vertical fluxes of nutrient-enriched drainage water in riparian zones. Trace element uptake differs significantly between
native plant species to the extent that selective planting on paddock borders may also add value through avoidance of deficiency diseases in stock. These potentially useful findings justify further research.

REFERENCES


TABLE AND FIGURE LEGENDS

Table 1. New Zealand native plant species of the present study. 1 Synonym = Austroderia richardii (Endl.) N.P. Barker and H.P. Linder (2010) [the current preferred name]; 2 Basionym = Leptospermum ericoides A.Rich (1832). Source: www.nzflora.landcareresearch.co.nz

Table 2. Chemical properties of paddock and research plot soils, and of pore water from two depths in the research plots at t0. Values are means ± standard deviations. For research plot soil, pH, C and N, n = 6 (mean values of the six native species); otherwise n = 5. For soluble elements, n = 10 (calculated from the reference sites of the research plot). Significant differences (>sd<) between adjacent values are indicated at P <0.05 where they exist. There were no significant differences in soil concentrations between species within the research plot. Blank spaces are undetermined variables.

Table 3. Soil and Plant species beneath which soil chemical concentrations (mg l⁻¹) were significantly higher or lower than in bare soil reference plots (n=10, reference sites; n=5 plant species).

Figure 1. The study site at the Lincoln University Dairy Farm. The sampling plot (A) is located in the corner of the dairy paddock, beyond the reach of the centre-pivot circular irrigator (B). Native plants were established in 2008. The dairy farm was converted from former dry sheep pasture in 2001, with the irrigation system installed soon after. The sampling plot is bordered by a drainage ditch (to the east) and a paved road (to the south). Image from GoogleEarth (2/15/2011, 43°38’38.1”S 172°26’02.19”E)

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Figure 3. Foliar concentrations of macronutrients. (Values are means ± s.e).
**Figure 4.** Foliar concentrations (Means ± s.e.) of trace elements. (Values are means ± s.e.).

**Figure 5.** Principal components analysis describing variation of foliar element concentrations in terms of plants species. The first two PCIs account for 74% of the data variation.

**Figure 6.** Soil pH (0-10cm) beneath native species compared to ryegrass in the research plot and paddock and bare soil in the plot (histogram bars, n=10 for the bare soil, n=5 all others). Symbols show pore water pH at the two depth of sampling (■15cm, □30cm, n=5). Arrow indicates falling pH with depth beneath bare soil.

**Figure 7.** Soil moisture beneath different plant species and reference locations on the plot at depths of 15 cm ( upper bars) and 30 cm depth ( lower bars). Values are means ± s.e. (n=5)

**Figure 8.** Nitrate concentrations in rhizon leachate samples from 15cm depth during the six sampling events over 11 weeks. Values are means ± s.e. (duplicate samples at each sampling event at each location).

**Figure 9.** Soil moisture and temperature during sampling events over the 11 week sampling period.
<table>
<thead>
<tr>
<th>English, Maori names</th>
<th>Family</th>
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<tbody>
<tr>
<td>black matipo, kohunu</td>
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</tr>
<tr>
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<td>Euphorbiaceae</td>
</tr>
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<td>toetoe</td>
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<td>monocephyteous flax, kahakate</td>
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</tr>
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<td>cabbage tree, ti cooka</td>
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</tr>
<tr>
<td></td>
<td>Paddock Soil</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td></td>
<td>pH</td>
</tr>
<tr>
<td></td>
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<tr>
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<tr>
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<tr>
<td>Zn</td>
<td>86.02 ± 1.73</td>
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</tbody>
</table>

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<td><strong>B</strong></td>
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<td>C. robusta</td>
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<table>
<thead>
<tr>
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<td>S</td>
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<td>Zn</td>
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</tr>
<tr>
<td>N</td>
<td>0.36</td>
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</table>

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