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CADMIUM ACCUMULATION IN CHICORY AND RYEGRASS WITH MODIFICATION OF SOIL pH

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Abstract

Field trials were established in two contrasting soils (Kereone [total Cd 1.12 mg kg^{-1}, pH 6.1]; and Topehaehae [total Cd 0.67 mg kg^{-1}, pH 6.1]) to evaluate the effect of soil pH modification on soil Cd phytoavailability and Cd accumulation in chicory (*Cichorium intybus*) and perennial ryegrass (*Lolium perenne*). Mean tissue Cd concentrations for chicory in both the Kereone and Topehaehae soils (2.265 and 2.701 mg kg^{-1} DM, respectively) were significantly ($P < 0.001$) greater than those for ryegrass (0.142 and 0.113 mg kg^{-1} DM, respectively). Ultra-fine elemental sulphur and hydrated lime treatments were effective in producing a wide range in soil pH (approximately 5.0-6.5) in both soils. There was a strong negative (linear) correlation between 0.05 M $CaCl_2$ soil extractable Cd concentration and pH in both soils (R^2 = 0.82 and 0.64 for the Kereone and Topehaehae soils, respectively). Correspondingly, plant tissue Cd concentrations were negatively correlated to soil pH (chicory R^2 = 0.52 and 0.35, and ryegrass R^2 = 0.42 and 0.19, for the Kereone and Topehaehae soils, respectively). However, the correlation between plant tissue Cd concentration and soil extractable Cd concentration was weak (R^2 = 0.11 and 0.28 for chicory and ryegrass, respectively), indicating that 0.05 M $CaCl_2$ soil extractable Cd is a poor predictor of soil Cd phytoavailability across different soil types. As ryegrass tissue Cd concentrations remained low (<0.3 mg kg^{-1}) across the entire pH range imposed, there appears little risk of increased animal dietary Cd exposure when grazing this plant species, even in Cd-enriched soils at low pH. In contrast, this trial indicates that soil pH should be increased to a minimum pH of 6.5 to decrease animal dietary Cd exposure risk when grazing chicory.

Introduction

Soil pH is generally considered to be the dominating factor influencing metal sorption and solubility in soils (Bolan et al., 1999; Christensen and Haung, 1999; Gray et al., 1999c; Loganathan et al., 2012; Young, 2012). Many researchers have shown increased heavy metal sorption and decreased solubility with increasing soil pH (Tiller et al., 1984; Boekhold et al., 1993; Naidu et al., 1994; Gray et al., 1998, 1999b, c; Srivastava et al., 2005; Vasconcelos et al., 2008). In particular, this is the case for soils dominated by variable charge clays and/or high organic matter content, since the specific sorption capacity of these soils will be more sensitive to change in pH (Bolan et al., 2003; Loganathan et al., 2012). Liming of acid soils is therefore considered one of the most practical and cost-effective means of decreasing plant tissue Cd accumulation (Bolan, 1996; Grant *et al.*, 1999; Young, 2012).

Despite the mechanisms between soil pH and Cd phytoavailability being proven under controlled glasshouse conditions (Maier *et al.*, 1997; Gray *et al.*, 1999b; Maier *et al.*, 2002) the effect of liming on plant Cd accumulation has often been inconsistent when tested in the field (Andersson and Siman, 1991; Sparrow *et al.*, 1993; Li *et al.*, 1996; Oliver *et al.*, 1996; Maier *et al.*, 1997; Maier *et al.*, 2002). This inconsistency may be explained by the time-delay for lime to reach its maximum effect on soil pH and Cd phytoavailability, or through differences in the depth / distribution of lime relative to Cd in the soil profile (Sparrow *et al.*, 1993; Sparrow and Salardini, 1997). Alternatively, as plant tissue Cd concentrations have been reported to be inversely related to plant growth rate / yield (Mortvedt *et al.*, 1981; Loganathan *et al.*, 1997; Roberts and Longhurst, 2002) it is possible that yield penalties from agronomically-undesirable increases in soil pH may override the concurrent decrease in soil Cd phytoavailability (Gray *et al.*, 1999b). Lastly, increases in soil solution calcium (Ca^{2+}) concentration following application of agricultural lime may increase competition between Ca^{2+} and Cd^{2+} for sorption sites, temporarily decreasing Cd^{2+} sorption and increasing its phytoavailability (Boekhold *et al.*, 1993; Bolan *et al.*, 2003).

New Zealand agricultural soils are weakly acidic, with soil pH typically falling within the range of 5.2-6.0 (Edmeades *et al.*, 1985; Morton *et al.*, 2005; Roberts and Morton, 2009). For this reason, liming to maintain soil pH at the upper end of the crop-specific recommended soil pH range has been advocated as a key strategy to reduce plant tissue Cd accumulation (FANZ, 2016). However, no field-based research has been carried out in New Zealand to evaluate the effectiveness of soil pH modification for controlling plant Cd accumulation under local conditions.

This information could be particularly important with regard to managing Cd phytoavailability and plant Cd accumulation for 'accumulator' crops such as chicory (Stafford *et al.*, 2016). Notably, data from a recent survey of plant tissue and soil samples collected from commercial farming properties across New Zealand (currently unpublished) revealed that soil pH was a significant ($P < 0.01$) predictor of tissue Cd concentration in chicory. Together with soil total Cd and total C, these three variables accounted for approximately 75% of the variability in chicory tissue Cd concentrations. The field research trial in this chapter was therefore undertaken to quantify the impact of soil pH modification on soil Cd phytoavailability and plant tissue Cd accumulation in chicory and ryegrass, under field conditions.

Methodology

Two trials were established on contrasting soils (Kereone silt loam and Topehaehae sandy clay loam (Table 1)) within a Waikato dairy farm. Suitable sites within these paddocks (e.g. uniform topography) were pegged out, with soil samples taken across the entirety of both trial areas.

Table 1. Description and characteristics of the soils at two trial site locations.

Soil type	Kereone silt loam	Topehaehae sandy clay loam
New Zealand Soil Classification (NZSC)	Typic Orthic Allophanic	Typic Recent Gley
Total Cd (mg kg^{-1})	1.12	0.67
Total P (mg kg^{-1})	1909	924
Total C (%)	6.7	3.3
P retention (%)	87	43
CEC (meq $100g^{-1}$)	26	17
pH	6.1	6.1
pH buffer capacity (mmol H^+ kg^{-1} pH^{-1})	29.4	16.8
Olsen-P (mg L^{-1})	19	20

Treatments and trial design

To establish a range of soil pH values at the two trials sites, powdered hydrated lime (Graymont lime; purity: 94% $Ca(OH)_2$, particle size: 90% < 90 µm) and ultra-fine elemental sulphur ('Kumulus' wettable sulphur fungicide (BASF); purity: 80% sulphur, particle size: 90% < 6 µm) were applied at the various rates as described in Table 2. Each treatment was represented by a single 4 m^2 plot (2 m x 2 m) with all 21 treatments in each site completely randomised within 3 rows of 7 plots.

Table 2. Treatments used in the two field trials and target soil pH values.

Treatment No.	Species	Alkali / acid treatment	$Ca(OH)_2$ (kg ha^{-1})	Elemental sulphur (kg ha^{-1})	Target pH
1	Chicory	Control			6.10
2	Chicory	0.5x alkali	370		6.16
3	Chicory	1x alkali	740		6.23
4	Chicory	2x alkali	1480		6.35
5	Chicory	3x alkali	2220		6.48
6	Chicory	4x alkali	2960		6.60
7	Chicory	0.5x acid		160	6.04
8	Chicory	1x acid		320	5.98
9	Chicory	2x acid		640	5.85
10	Chicory	3x acid		960	5.73
11	Ryegrass	Control			6.10
12	Ryegrass	0.5x alkali	370		6.16
13	Ryegrass	1x alkali	740		6.23
14	Ryegrass	2x alkali	1480		6.35
15	Ryegrass	3x alkali	2220		6.48
16	Ryegrass	4x alkali	2960		6.60
17	Ryegrass	0.5x acid		160	6.04
18	Ryegrass	1x acid		320	5.98
19	Ryegrass	2x acid		640	5.85
20	Ryegrass	3x acid		960	5.73
21	Fallow	-			6.10

Soil pH buffer capacity analysis was initially undertaken on the two soils to determine the required alkali/acid inputs to shift pH. However, these theoretical calculations indicated much lower rates of lime were required to adjust pH than that typically observed (Morton *et al.*, 1998; Morton *et al.*, 2005; Moir and Moot, 2014), therefore this approach was abandoned. Instead, the maximum application rate of hydrated lime was based upon a targeted maximum increase in soil pH of 0.5 units (0-75 mm depth), which as a generalisation typically requires 4000 kg ha^{-1} $CaCO_3$-equivalent (i.e. 5000 kg ha^{-1} agricultural lime assuming 80% $CaCO_3$) (Roberts and Morton, 2009). All other hydrated lime and ultra-fine elemental sulphur rates (providing equivalent OH^-/H^+ inputs) were sequentially decreased from this maximum rate of hydrated lime so as to vary the influence on soil pH relative to that in the control plots.

Management

On 11 September 2015 the two trial sites were fenced-off and the existing pastures were sprayed with the herbicides Zero® (Yates; 490 g kg^{-1} glyphosate) and Turfix® (Yates; 200 g L^{-1} mecoprop, 50 g L^{-1} MCPA and 6.2 g L^{-1} dicamba) at 8 mL ha^{-1} and 13 L ha^{-1}, respectively. On 26 September 2015, lawnmowers were used to trim off any remaining pasture residues (to approximately 25 mm height). Plots were then pegged out in both trial areas forming 3 rows of 7 plots, with an unplanted 1 m buffer between plots and a 2 m buffer around the outside perimeter of the trial area. Hydrated lime and elemental sulphur treatments were then applied by hand to the relevant plots. Basal fertiliser (triple superphosphate and potassium sulphate, supplying 21 kg P ha^{-1}, 124 kg K ha^{-1} and 50 kg S ha^{-1}) was then applied

to each plot to encourage plant establishment and support growth over the duration of the trial. No nitrogen fertiliser was applied; this was deemed unnecessary given soils cultivated out of ryegrass-white clover pasture typically have high N-mineralisation capacity (Francis et al., 1992).

All plots were then cultivated to approximately 75 mm depth using a self-driven rotary hoe (with the exception of one plot in each site that was retained as an unplanted fallow treatment). Diploid perennial ryegrass (Excess® (PGG Wrightson seeds) with AR 37® endophyte and Superstrike® insecticide coating) and chicory (Choice® (Grasslands seeds) with Superstrike® insecticide coating) seeds were then mixed with soil (to act as a carrier and aid dispersal) and then applied by hand to appropriate plots, at 20 and 6 kg ha^{-1}, respectively. All plots were then raked to work the applied seed into the soil, and then plots were pressed to improve seed-to-soil contact using a hand roller. Finally, Blitzem® slugbait (Yates; 15 g kg^{-1} metaldehyde) was applied at 10 kg ha^{-1} to avoid slug damage to emerging seedlings.

Plots were inspected on 10 October 2015, with emergence of both plant species appearing relatively uniform. Seed was applied by hand to small areas of some plots to bolster plant populations where initial establishment was poor. On the 26 October, plots containing chicory were sprayed with Valdo® (Nufarm; 800 g kg^{-1} flumetsulam) at 65 g ha^{-1} and Sequence® (Nufarm; 240 g L^{-1} clethodim) at 500 mL ha^{-1} to control broadleaf and grass weeds, respectively. Plots containing ryegrass seedlings received the herbicide Tribal Gold® (Nufarm; 300 g L^{-1} MCPB, 20 g L^{-1} MCPA and 10 g L^{-1} flumetsulam) at 5 L ha^{-1} to control broadleaf weeds. All herbicides were tank-mixed with Bonza® surfactant (Nufarm; 471 g L^{-1} heavy paraffinic petroleum distillate) at 5 mL L^{-1} water, and then applied at 150 L ha^{-1} using a hand-held boom sprayer fitted with flat fan nozzles. Throughout the duration of the trial, non-vegetated buffer zones between plots and surrounding the entire trial area were maintained using the herbicides Zero® (Yates; 490 g kg^{-1} glyphosate) and Turfix® (Yates; 200 g L^{-1} mecoprop, 50 g L^{-1} MCPA and 6.2 g L^{-1} dicamba) at 8 mL ha^{-1} and 13 L ha^{-1}, respectively.

Plant tissue harvests

Three plant tissue harvests took place through the trial duration, occurring on 18 November, 11 December and 28 December 2015. At each harvest, each treatment plot was split into four 1 m x 1 m sub-plot areas, allowing four plant tissue replicates to be collected for Cd concentration analysis per treatment. Chicory replicates consisted of ten entire plants (typically 100-300 g fresh weight (FW)) harvested at 30 mm height from five sub-sampling points within the 1 m^2 sub-plot area (i.e. 2 plants per sub-sampling point). Ryegrass replicates (typically 50-150 g FW) were harvested with hand shears, collecting the leaf and stem tissue from two parallel strips approximately 500 mm in length (harvested to 30 mm height) within each sub-plot area, which were then bulked into a single sample per replicate.

Soil sampling

At the completion of the third (final) plant tissue harvest, the effect of each alkali/acid treatment on soil pH and extractable Cd concentration was assessed. Five soil cores (0-150 mm depth) were collected and combined within each 1 m^2 sub-plot area, providing four replicates per treatment. These samples were also immediately couriered to Massey University for extractable Cd concentration and pH analysis.

Results and Discussion

Main effect of soil type and plant species

Using data from control plots only, the mean soil extractable Cd concentration was shown to be significantly (P = 0.002) greater for the Kereone than the Topehaehae soil, despite there being no significant difference (P = 0.057) in soil pH (Table 3). The greater soil extractable Cd concentration of the Kereone soil is consistent with its much greater soil total Cd concentration (Table 1).

Table 3. Comparison between soil types ('control' replicates only) of mean soil pH and extractable Cd concentration (assessed at final harvest) and mean tissue Cd concentrations for ryegrass and chicory (assessed using data from all 3 harvests).

Variable	Soil type		*P* value
	Kereone	Topehaehae	
Mean soil pH	6.07	5.94	0.057
Mean extractable Cd conc. (mg kg $^{-1}$)	0.105	0.063	0.002
Mean ryegrass Cd conc. (mg kg $^{-1}$ DM)	0.111	0.062	0.036
Mean chicory Cd conc. (mg kg $^{-1}$ DM)	1.643	2.413	0.217
P value (chicory vs ryegrass)	<0.001	<0.001	

Mean tissue Cd concentrations in control plots were much greater (P < 0.001) for chicory (1.643-2.413 mg kg^{-1} DM) than ryegrass (0.062-0.111 mg kg^{-1} DM) (Table 3). Ryegrass mean tissue Cd concentration was significantly (P = 0.036) greater in the Kereone than the Topehaehae soil, consistent with the greater soil extractable Cd concentration of the Kereone soil. Mean chicory tissue Cd concentration was not significantly different (P = 0.217) between the two soil types.

Effect of soil amendments on soil pH

Relative to the control plots, elemental sulphur treatments drove significant (P < 0.05) reductions in soil pH for both soil types (Figure 1). In contrast however, hydrated lime treatments had little impact on increasing soil pH, with only the highest rate of hydrated lime ('4x lime') in the Topehaehae soil driving a significant (P < 0.05) increase in soil pH relative to the control pH (Figure 1.b). Overall, fewer treatments generated significant (P < 0.05) changes in pH within the Kereone soil (Figure 1.a) than the Topehaehae soil (Figure 1.b), reflecting the stronger pH buffering capacity of the Kereone soil (Table 1).

The overall lack of a significant effect on soil pH from the hydrated lime treatments was unexpected. Hydrated lime has been successfully used by previous authors (Chaney *et al.*, 1977; Gray *et al.*, 1999b; Bolan *et al.*, 2003) to overcome the low solubility of agricultural limestone ($CaCO_3$) and its consequent lag-effect on Cd phytoavailability within the year of application (Sparrow *et al.*, 1993; Sparrow and Salardini, 1997). The maximum hydrated lime application rate used (4000 kg ha^{-1} $CaCO_3$-equivalent) was much greater than the theoretical $CaCO_3$-equivalent requirement to shift pH by 0.5 unit that was derived for the Kereone soil (849 kg ha^{-1}) and the Topehaehae soil (568 kg ha^{-1}) from the pH buffer capacity analysis. The lack of impact on soil pH from hydrated lime relative to that from elemental sulphur may be the consequence of ongoing soil acidification effects related to enhanced soil organic matter mineralisation, nitrification and nitrate leaching processes following cultivation (Ridley *et al.*, 1990; Bolan *et al.*, 1991; McLaren and Cameron, 1996).

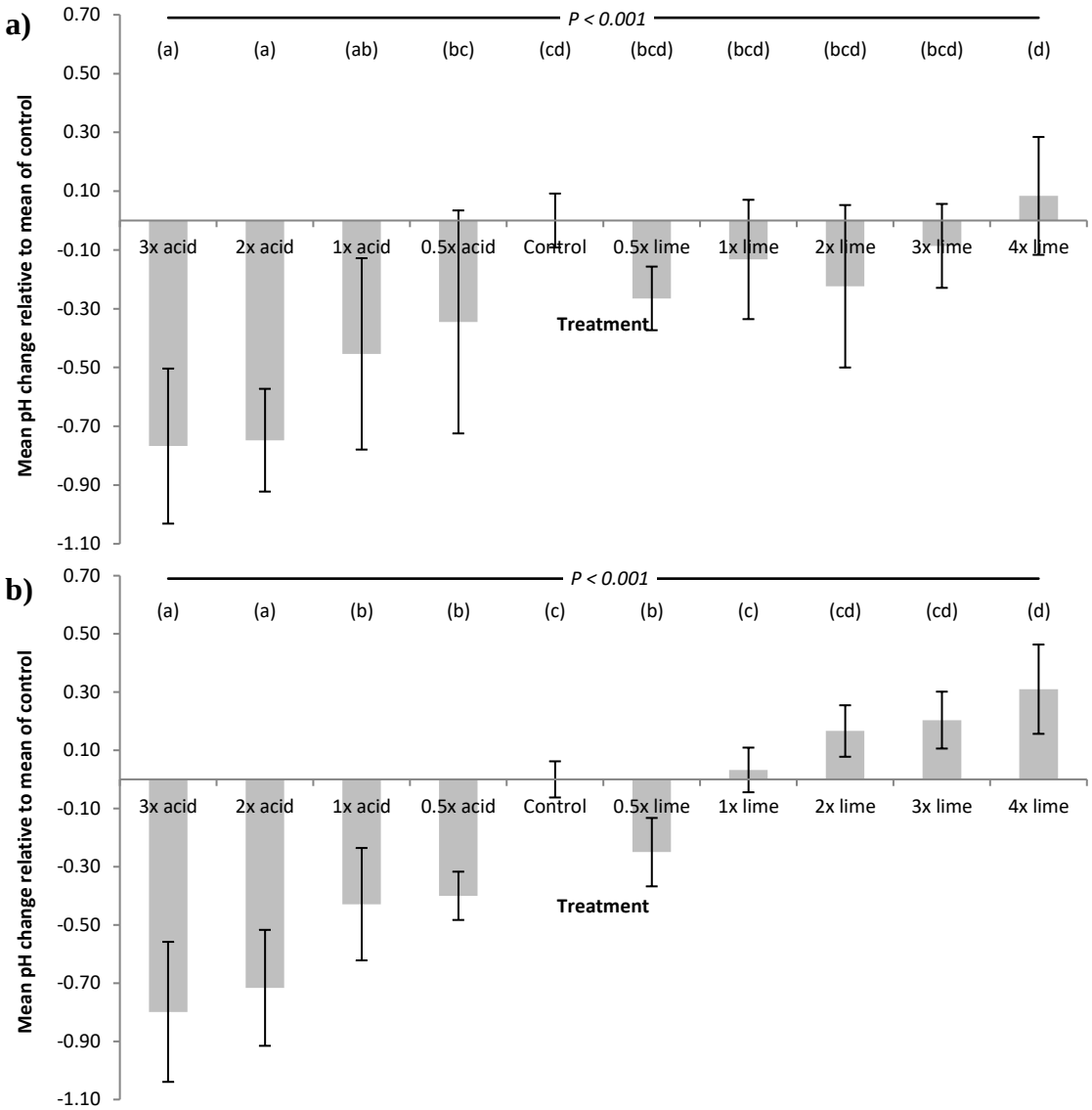

Figure 1. Mean change in soil pH for each acid/alkali treatment replicate relative to the mean pH of control, assessed across plant species within each site (n = 8 for each treatment). **a)** Kereone soil, and **b)** Topehaehae soil. Error bars represent the standard deviation. Means with the same letter indicate differences are not significant ($P < 0.05$).

Relationship between soil extractable Cd concentration and pH

Despite the lack of impact on soil pH from the hydrated lime treatments, the desired wide range in soil pH (5.0-6.5) was still achieved in both soils (Figure 2). A significant ($P < 0.001$) negative linear correlation between soil extractable Cd concentration and soil pH, with this relationship being slightly tighter for the Kereone soil ($R^2 = 0.82$) than the Topehaehae soil ($R^2 = 0.64$). This inverse relationship is expected, since metal specific sorption capacity in variable charge soils is known to increase within increasing soil pH, with a concurrent reduction in Cd solubility (Tiller *et al.*, 1984; Naidu *et al.*, 1994; Bolan *et al.*, 2003; Srivastava *et al.*, 2005).

The change in extractable Cd concentration per unit change in soil pH was very similar for both soil types. At equivalent soil pH, the greater extractable Cd concentration of the Kereone soil relative to the Topehaehae soil (Figure 2) is consistent with the greater total Cd concentration of the Kereone soil (Table 1).

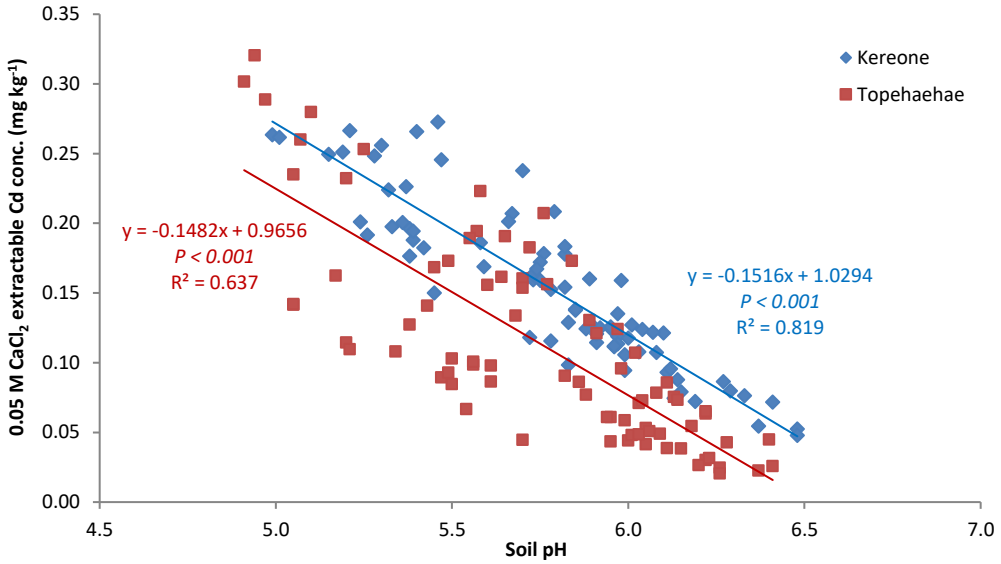

Figure 2. Relationship between soil extractable Cd concentration and soil pH for the Kereone and Topehaehae soil types.

Relationship between plant tissue Cd concentration, soil pH and extractable Cd concentration

Chicory

The relationship between chicory tissue Cd concentration and soil pH (isolated to individual soil types) or 0.05 M $CaCl_2$ extractable Cd concentration (soil types combined) is shown in Figure 3.a and Figure 3.b, respectively. Tissue Cd concentration decreased with increasing soil pH (Figure 3.a) although the coefficient of determination was only weak to moderate (R^2 = 0.52 and 0.35 for the Kereone and Topehaehae soils respectively). This trend is consistent with a decrease in soil Cd phytoavailability as indicated by the relationship between soil pH and soil extractable Cd concentration in Figure 2. Although chicory tissue Cd concentration (across both soils combined) was positively correlated to soil extractable Cd concentration (Figure 3.b) the coefficient of determination was very poor (R^2 = 0.11).

Ryegrass

The relationship between chicory tissue Cd concentration and soil pH (isolated to individual soil types) or 0.05 M $CaCl_2$ extractable Cd concentration (soil types combined) is shown in Figure 4.a and Figure 4.b, respectively. Similar to chicory, ryegrass Cd concentration decreased with increasing soil pH (Figure 4.a) however the gradient of this relationship was less steep for ryegrass than chicory, indicating that soil pH had a smaller influence on tissue Cd concentration in ryegrass. In addition, for both soil types, the coefficient of determination between ryegrass Cd concentration and soil pH (R^2 = 0.42 and 0.19 for the Kereone and Topehaehae soils, respectively) was weaker than that for chicory. Across both soil types combined there was a positive relationship between ryegrass tissue Cd concentration and 0.05 M $CaCl_2$ soil extractable Cd concentration (Figure 4.b), however the correlation was poor (R^2 = 0.28).

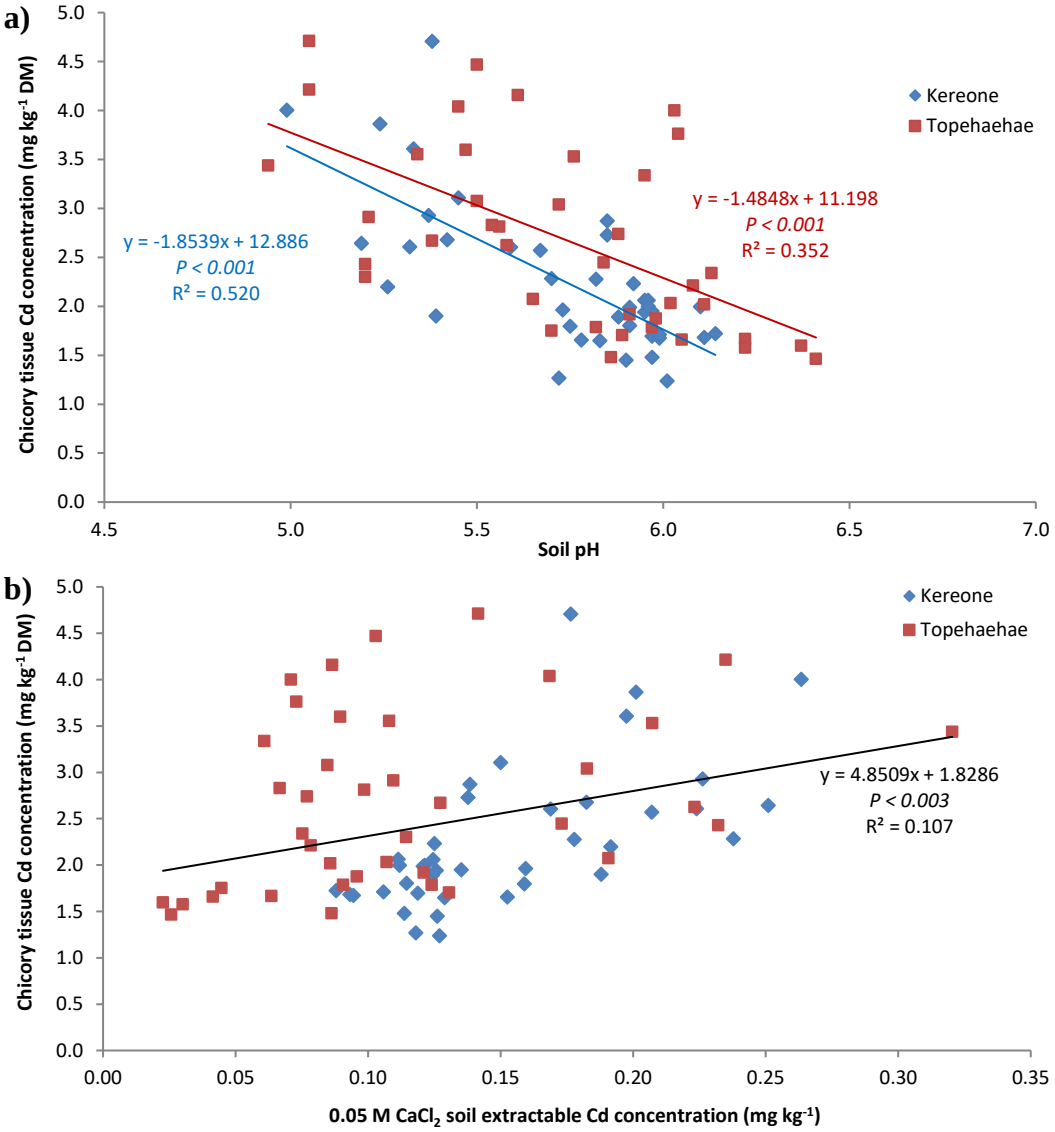

Figure 3. Relationship between chicory tissue Cd concentration and **a)** soil pH for the Kereone and Topehaehae soils independently, and **b)** soil extractable Cd concentration across the Kereone and Topehaehae soils combined.

The relationship between plant tissue Cd concentration and soil pH or soil extractable Cd concentration (Figure 3 and Figure 4) is considerably weaker than that between soil extractable Cd concentration and soil pH. In part, this may be related to greater natural 'biological' variability when analysing plant tissue, for example dilution effects due to differences in growth rate (Mortvedt *et al.*, 1981; Mortvedt, 1987) and/or variation in Cd uptake and internal translocation efficiency (Welch and Norvell, 1999) between plant samples analysed. In addition, an important factor is that the plant root network exploits a much greater area of soil than that represented by soil sample 'point-analysis'. With varying rainfall and soil moisture, plant metal uptake may also vary based on relative Cd concentration in soil zones from where plant roots are actively drawing moisture and other nutrients (Williams and David, 1977; Manschadi et al., 2013).

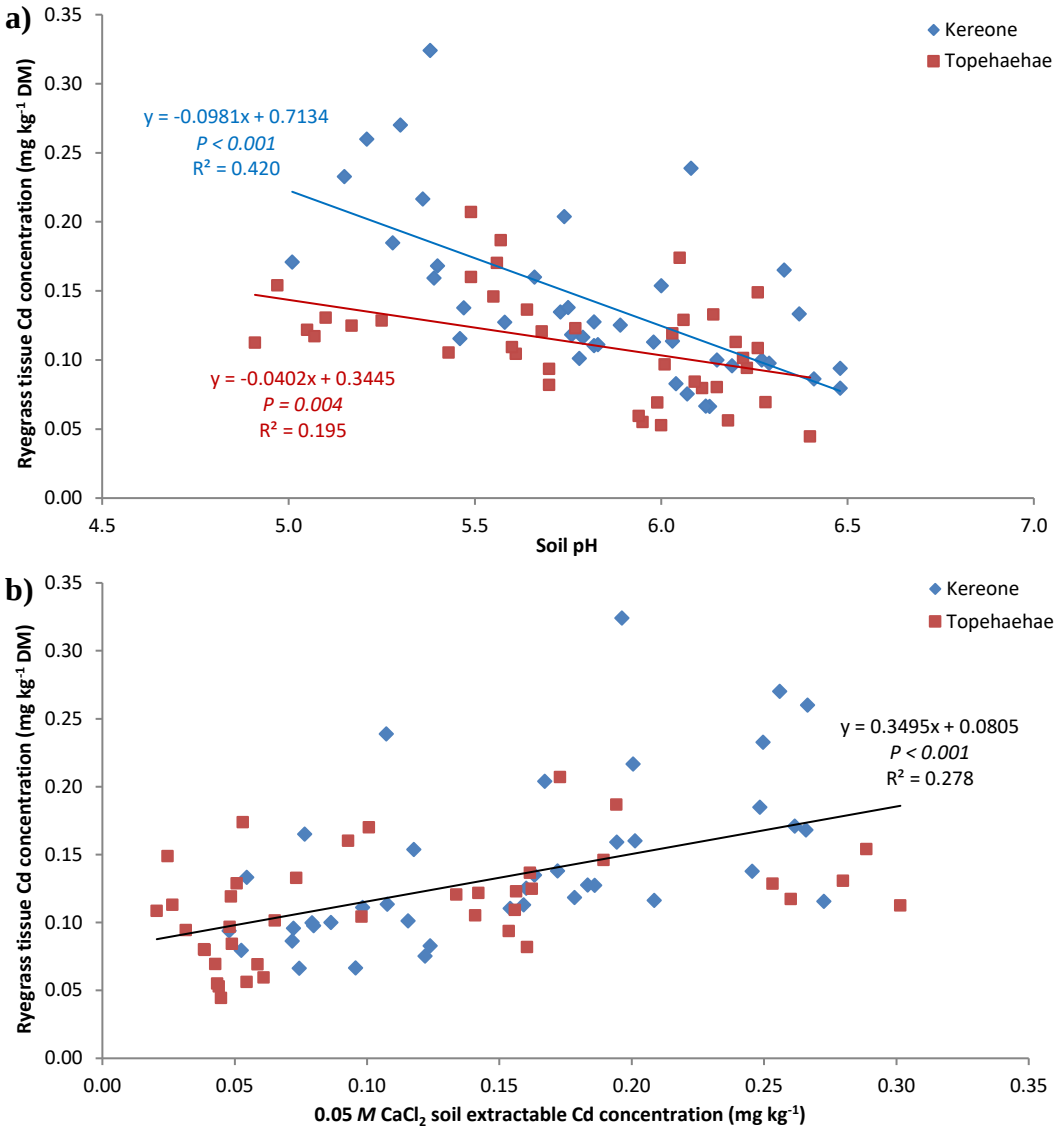

Figure 4. Relationship between ryegrass tissue Cd concentration and **a)** soil pH for the Kereone and Topehaehae soils independently, and **b)** soil extractable Cd concentration across the Kereone and Topehaehae soils combined.

The poor correlation between 0.05 M $CaCl_2$ extractable soil Cd and plant tissue Cd concentrations overall (Figure 3.b and Figure 4.b) indicates 0.05 M $CaCl_2$ extractable soil Cd is an unreliable predictor of soil Cd phytoavailability and plant tissue Cd accumulation, for either ryegrass or chicory. Although previous research has reported this extractant to be strongly correlated with ryegrass Cd concentration (Andrewes *et al.*, 1996; Gray *et al.*, 1999a, b; Roberts and Longhurst, 2002) most of this research has been undertaken under controlled laboratory conditions, using a wide range of soils with contrasting characteristics (clay mineralogy, pH, organic matter and total Cd concentration) that influence Cd phytoavailability (Andrewes *et al.*, 1996; Gray *et al.*, 1999a, b). Drawing a robust relationship between plant tissue Cd concentration and soil extractable Cd concentration is likely to be more challenging under field conditions, where there is greater background variation than in pot trials. For example, Roberts *et al.* (1995) reported poor correlation between 0.05 M $CaCl_2$ soil extractable Cd concentration and tissue Cd concentrations in market garden crops (R^2 = 0.17) and wheat grain (R^2 = 0.04), although the authors did not attempt to correct for variation that is likely to exist between species or cultivars (Adriano,

1986; McLaughlin *et al.*, 1994; Gray *et al.*, 1999b). Although Roberts and Longhurst (2002) reported 0.05 M $CaCl_2$ extractable soil Cd to account for 94% of the variability in pasture Cd concentrations in their field study, different coefficients were needed for different slope classes. Similar challenges have been found for other extractants. For example, 0.05 M $Ca(NO_3)_2$ has shown to be a good predictor of Cd phytoavailability in controlled pot trials (Gray *et al.*, 1999a, b), however Reiser *et al.* (2014) reported that it was relatively weakly correlated (Spearmans *rho* = 0.41) to pasture Cd concentration across a range of field survey sites.

Previous research into various soil Cd extractants (including 0.05 M $CaCl_2$) has also reported wide variation in the correlation with tissue Cd concentration when the extractants were assessed across different plant species (Gray *et al.*, 1999a, b). This could explain the poor correlation with chicory tissue Cd concentrations observed in this trial, since this plant species has not been previously tested. Justification for the use of 0.05 M $CaCl_2$ for soil extractable Cd assessment in this study was based on its previous usage, and reported strong correlation with ryegrass Cd concentration (Andrewes *et al.*, 1996; Gray *et al.*, 1999a, b; Roberts and Longhurst, 2002). In addition, it is a relatively weak extractant with low pH buffering capacity, characteristics that are considered favourable for prediction of Cd phytoavailability, since the extractant is likely to be more sensitive to change in soil pH (Gray *et al.*, 1999a, b). Given the focus on manipulation of soil pH on soil Cd phytoavailability in this study, this was considered a critical characteristic.

Implications for agricultural management

The significantly ($P < 0.001$) greater mean tissue Cd concentration for chicory than ryegrass determined in this trial is consistent with, and further validates, data from an earlier glasshouse trial (Stafford *et al.*, 2016). In addition, the ryegrass Cd concentration ranges determined in this trial (typically less than 0.3 mg kg^{-1} DM) are consistent with the literature (Roberts et al., 1994; Loganathan et al., 1995; Loganathan et al., 1997; Roberts and Longhurst, 2002; Gray and McLaren, 2005; Reiser et al., 2014).

As Cd accumulation in the liver and kidney of grazing livestock is dependent on dietary Cd intake (Lee *et al.*, 1994; Lee *et al.*, 1996), the much greater tissue Cd concentration of chicory has the potential to increase the rate of Cd accumulation in the liver and kidney of grazing livestock (Stafford *et al.*, 2016) potentially resulting in greater exceedance of food standard MLs for these animal tissues.

As sorption of Cd is expected to increase in variable charge soils with increasing pH (Tiller *et al.*, 1984; Naidu *et al.*, 1994; Srivastava *et al.*, 2005) liming is traditionally viewed as one of the most practical means for reducing soil Cd phytoavailability (Young, 2012). The linear decrease in soil extractable Cd concentration with increasing soil pH demonstrated in this field trial (Figure 2) is consistent with previous research showing Cd solubility / extractable Cd concentration to be negatively correlated to soil pH (He and Singh, 1993; McBride *et al.*, 1997; Gray *et al.*, 1998, 1999c). However, while tissue Cd concentrations for both chicory (Figure 3) and ryegrass (Figure 4) also correspondingly decreased with increasing pH, this relationship was comparatively much weaker (R^2 = 0.19-0.52) than that between soil extractable Cd concentration and soil pH (R^2 = 0.64-0.82).

Within this field trial, ryegrass had low (<0.3 mg kg^{-1} DM) tissue Cd concentrations even at a pH of 5.0. Consistent with this, analysis of data from the previous field survey carried out within this thesis did not find pH to be a significant predictor of ryegrass tissue Cd

concentration. As most New Zealand pastures are typically managed within a pH range of 5.2-6.0 (Edmeades *et al.*, 1985; Morton *et al.*, 2005; Roberts and Morton, 2009) this supports previous research that suggested animal Cd accumulation risk is relatively low for livestock grazing ryegrass / white clover pastures (Loganathan *et al.*, 1999; Reiser *et al.*, 2014). It also suggests that pH manipulation is not likely to greatly influence animal Cd accumulation when grazing ryegrass-based pasture.

Manipulation of soil pH had a stronger effect on tissue Cd concentrations in chicory in this trial, consistent with data from the previous field crop survey that indicated that tissue Cd concentrations in chicory were significantly ($P < 0.01$) influenced by soil pH (as well as total C and Cd concentrations). Regression data from the current field trial shows that chicory tissue Cd concentrations changed by approximately 1.5-1.9 mg kg^{-1} DM (depending on soil type) for every 1.0 unit change in soil pH (Figure 3.a). This illustrates the risk of greater livestock dietary Cd exposure for this plant species that could be brought about by an unintentional decline in soil pH over time. This could arise through under-application of lime at/prior to sowing, in combination with enhanced organic matter mineralisation post-cultivation, and increased nitrification and nitrate leaching driven by N-fertiliser and concentrated stock urine deposition (Ridley *et al.*, 1990; Bolan *et al.*, 1991; McLaren and Cameron, 1996).

Alternatively, it also indicates the potential to manage Cd accumulation in chicory by increasing soil pH. Although it would not be normal agricultural practice to increase soil pH beyond 6.0 since yield responses to further lime inputs are seldom economic (Edmeades *et al.*, 1985), the exception to this could be for the specific purpose of reducing tissue Cd accumulation in Cd-sensitive species such as chicory. For example, based on the relationships in Figure 3.a and an agronomically-realistic increase in soil pH from 5.5 to 6.5, chicory tissue Cd concentration would be decreased by 49-69%. This is comparable to the mean 60% reduction in tissue Cd concentration (across 5 plant species and 3 soil types) in glasshouse-based research reported by Gray *et al.* (1999b) as a consequence of increasing soil pH from 5.5 to 7.0. Field trials have generally shown smaller and or more variable effects on plant tissue Cd accumulation from manipulation of soil pH than glasshouse pot-trial research (Li *et al.*, 1996; Oliver *et al.*, 1996; Maier *et al.*, 1997; Maier *et al.*, 2002). However, Sparrow and Salardini (1997) indicated a 24% decrease in mean potato tuber Cd concentrations per 1.0 unit increase in soil pH. In addition, Guttormsen *et al.* (1995) reported mean tissue Cd concentrations for Chinese cabbage and carrots to be 23% and 46% greater (respectively) at a soil pH of 5.5 relative to 6.5, while He and Singh (1993) reported an approximate 40% reduction in Cd concentration in mixed-grass samples at pH of 6.5 compared to 5.5.

Ultimately, an indicator of soil Cd phytoavailability is required for Cd sensitive crops, to allow for simple and direct risk-analysis across different soil types that have differing Cd sorption / solubility characteristics. Unfortunately, 0.05 M $CaCl_2$ soil extractable Cd concentration assessed to 150 mm soil depth did not provide a reliable relationship with chicory tissue Cd concentration across the soil types in this study.

Conclusions

The significant ($P < 0.001$, $R^2 = 0.64$-0.82) negative correlation between soil pH and 0.05 M $CaCl_2$ soil extractable Cd concentration in this trial reinforces that soil pH is an important factor influencing soil Cd phytoavailability. Correspondingly, plant tissue Cd concentrations were negatively correlated to soil pH (chicory $R^2 = 0.52$ and 0.35, and ryegrass $R^2 = 0.42$ and 0.19, for the Kereone and Topehaehae soils, respectively). However, soil extractable Cd

concentration was unable to explain much of the variability in chicory or ryegrass tissue Cd concentrations (R^2 = 0.11 and 0.28, respectively), indicating that 0.05 M $CaCl_2$ soil extractable Cd is a poor predictor of soil Cd phytoavailability across different soil types. Ryegrass tissue Cd concentrations were significantly ($P < 0.001$) lower than those of chicory, and remained low (generally <0.3 mg kg^{-1} DM) even in the Cd-enriched Kereone soil (1.12 mg kg^{-1} DW) at low pH (<5.5). This suggests animal Cd accumulation risk is very low when grazing ryegrass dominant pasture, particularly since Cd-enriched soils primarily occur in lowland, intensive agricultural soils where lime is regularly applied to maintain soil pH at around 6.0. In contrast, chicory tissue Cd concentrations were sensitive to soil pH, with regression analysis indicating a mean decrease in tissue Cd concentration of approximately 1.5-1.9 mg kg^{-1} DM per unit pH increase. Increasing soil pH to a minimum of 6.5 is a practical and simple management practice to reduce livestock dietary Cd exposure risk when grazing chicory.

References

Adriano, D.C., 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York, USA. 533 p.

Andersson, A., Siman, G., 1991. Levels of cadmium and some other trace elements in soils and crops as influenced by lime and fertiliser level. Acta Agriculturae Scandinavica 41, 3-11.

Andrewes, P., Town, R.M., Hedley, M.J., Loganathan, P., 1996. Measurement of plant-available cadmium in New Zealand soils. Australian Journal of Soil Research 34, 441-452.

Boekhold, A.E., Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., 1993. Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. Journal of Soil Science 44, 85-96.

Bolan, N.S., 1996. Cadmium accumulation in New Zealand pasture soils. Chemistry in New Zealand 60, 33-39.

Bolan, N.S., Adriano, D.C., Mani, P.A., Duraisamy, A., 2003. Immobilization and phytoavailability of cadmium in variable charge soils. II. Effect of lime addition. Plant & Soil 251, 187-198.

Bolan, N.S., Hedley, M.J., White, R.E., 1991. Processes of soil acidification during nitrogen cycling with emphasis on legume based pastures. Plant and Soil 134, 53-63.

Bolan, N.S., Naidu, R., Syers, J.K., Tillman, R.W., 1999. Surface charge and solute interactions in soils. Advances in Agronomy 67, 88-141.

Chaney, W.R., Strickland, R.C., Lamoreaux, R.J., 1977. Phytotoxicity of cadmium inhibited by lime. Plant and Soil 47, 275-278.

Christensen, T.H., Haung, P.M., 1999. Solid phase cadmium and the reactions of aqueous cadmium with soil surfaces. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 65-96.

Edmeades, D.C., Pringle, R.M., Mansell, G.P., Shannon, P.W., Ritchie, J., Stewart, K.M., 1985. Effects of lime on pasture production on soils in the North Island of New Zealand. 5. Description of a lime recommendation scheme. New Zealand Journal of Experimental Agriculture 13, 47-58.

FANZ, 2016. Tiered Fertiliser Management System for the management of soil cadmium accumulation from phosphate fertiliser applications. Version 2, June 2016. Fertiliser Association of New Zealand. Wellington, New Zealand. 12 p. http://www.fertiliser.org.nz/Site/resource_center/Tech_Papers.aspx.

Francis, G.S., Haynes, R.J., Sparling, G.P., Ross, D.J., Williams, P.H., 1992. Nitrogen mineralization, nitrate leaching and crop growth following cultivation of a temporary leguminous pasture in autumn and winter. Fertilizer Research 33, 59-70.

Grant, C.A., Bailey, L.D., McLaughlin, M.J., Singh, B.R., 1999. Management factors which influence cadmium concentration in crops. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 151-198.

Gray, C.W., McLaren, R.G., 2005. The effect of ryegrass variety on trace metal uptake. New Zealand Journal of Agricultural Research 48, 285-292.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1998. Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. Australian Journal of Soil Research 36, 199-216.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1999a. Cadmium phytoavailability in some New Zealand soils. Australian Journal of Soil Research 37, 461-477.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1999b. Effect of soil pH on cadmium phytoavailability in some New Zealand soils. New Zealand Journal of Crop and Horticultural Science 27, 169-179.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1999c. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. European Journal of Soil Science 50, 127-137.

Guttormsen, G., Singh, B.R., Jeng, A.S., 1995. Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertilizer and soil pH. Fertilizer Research 41, 27-32.

He, Q.B., Singh, B.R., 1993. Plant availability of cadmium in soils: II. Factors related to the extractability and plant uptake of cadmium in cultivated soils. Acta Agriculturae Scandinavica Section B: Soil and Plant Science 43, 142-150.

Lee, J., Grace, N.D., Rounce, J.R., 1994. Cadmium accumulation in liver and kidney of sheep grazing ryegrass/white clover pastures. Proceedings of the New Zealand Society of Animal Production 54, 31-34.

Lee, J., Rounce, J.R., Mackay, A.D., Grace, N.D., 1996. Accumulation of cadmium with time in Romney sheep grazing ryegrass-white clover pasture: effect of cadmium from pasture and soil intake. Australian Journal of Agricultural Research 47, 877-894.

Li, Y.M., Chaney, R.L., Schneiter, A.A., Johnston, B.L., 1996. Effect of field limestone applications on cadmium content of sunflower (*Helianthus annuus* L.) leaves and kernels. Plant and Soil 180, 297-302.

Loganathan, P., Hedley, M.J., Gregg, P.E.H., Currie, L.D., 1997. Effect of phosphate fertiliser type on the accumulation and plant availability of cadmium in grassland soils. Nutrient Cycling in Agroecosystems 47, 169-178.

Loganathan, P., Louie, K., Lee, J., Hedley, M.J., Roberts, A.H.C., Longhurst, R.D., 1999. A model to predict kidney and liver cadmium concentrations in grazing animals. New Zealand Journal of Agricultural Research 42, 423-432.

Loganathan, P., Mackay, A.D., Lee, J., Hedley, M.J., 1995. Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertilizer application and sheep grazing. Australian Journal of Soil Research 33, 859-871.

Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2012. Cadmium Sorption and Desorption in Soils: A Review. Critical Reviews in Environmental Science and Technology 42, 489-533.

Maier, N.A., McLaughlin, M.J., Heap, M., Butt, M., Smart, M.K., 2002. Effect of current-season application of calcitic lime and phosphorus fertilization on soil pH, potato growth, yield, dry matter content, and cadmium concentration. Communications in Soil Science & Plant Analysis 33, 2145-2165.

Maier, N.A., McLaughlin, M.J., Heap, M., Butt, M., Smart, M.K., Williams, C.M.J., 1997. Effect of current-season application of calcitic lime on soil pH, yield and cadmium concentration in potato (*Solanum tuberosum* L.) tubers. Nutrient Cycling in Agroecosystems 47, 29-40.

Manschadi, A.M., Manske, G.G.B., Vlek, P.L.G., 2013. Root architecture and resource acquisition: wheat as a model plant. In: Eshel, A., Beeckman, T. (Eds.), Plant roots : the hidden half (4th Edition). CRC Press, Boca Raton, Florida, pp. 1-18.

McBride, M., Sauve, S., Hendershot, W., 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. European Journal of Soil Science 48, 337-346.

McLaren, R.G., Cameron, K.C., 1996. Soil science : sustainable production and environmental protection. Oxford University Press, Auckland, New Zealand. 304 p.

McLaughlin, M.J., Williams, C.M.J., McKay, A., Kirkham, R., Gunton, J., Jackson, K.J., Thompson, R., Dowling, B., Partington, D., Smart, M.K., Tiller, K.G., 1994. Effect of cultivar on uptake of cadmium by potato tubers. Australian Journal of Agricultural Research 45, 1483-1495.

Moir, J.L., Moot, D.J., 2014. Medium-term soil pH and exchangeable aluminium response to liming at three high country locations. Proceedings of the New Zealand Grasslands Association 76, Alexandra, New Zealand, pp. 41-46.

Morton, J.D., Gray, M.H., Gillingham, A.G., 2005. Soil and pasture responses to lime on dry hill country in central Hawke's Bay, New Zealand. New Zealand Journal of Agricultural Research 48, 143-150.

Morton, J.D., Wheeler, D.M., Smith, N.S., 1998. Effect of lime and form of superphosphate on productivity of dryland pastures. New Zealand Journal of Agricultural Research 41, 65-74.

Mortvedt, J.J., 1987. Cadmium levels in soils and plants from some long-term soil fertility experiments in the United States of America. Journal of Environmental Quality 16, 137-142

Mortvedt, J.J., Mays, D.A., Osborn, G., 1981. Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers. Journal of Environmental Quality 10, 193-197.

Naidu, R., Bolan, N.S., Kookana, R.S., Tiller, K.G., 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. European Journal of Soil Science 45, 419-429.

Oliver, D.P., Tiller, K.G., Conyers, M.K., Slattery, W.J., Alston, A.M., Merry, R.H., 1996. Effectiveness of liming to minimise uptake of cadmium by wheat and barley grain grown in the field. Australian Journal of Agricultural Research 47, 1181-1193.

Reiser, R., Simmler, M., Portmann, D., Clucas, L., Schulin, R., Robinson, B., 2014. Cadmium concentrations in New Zealand pastures: relationships to soil and climate variables. Journal of Environmental Quality 43, 917-925.

Ridley, A.M., Slattery, W.J., Helyar, K.R., Cowling, A., 1990. Acidification under grazed annual and perennial grass based pastures. Australian Journal of Experimental Agriculture 30, 539-544.

Roberts, A.H.C., Longhurst, R.D., 2002. Cadmium cycling in sheep-grazed hill-country pastures. New Zealand Journal of Agricultural Research 45, 103-112.

Roberts, A.H.C., Longhurst, R.D., Brown, M.W., 1994. Cadmium status of soils, plants, and grazing animals in New Zealand. New Zealand Journal of Agricultural Research 37, 119-129.

Roberts, A.H.C., Longhurst, R.D., Brown, M.W., 1995. Cadmium survey of South Auckland market gardens and Mid Canterbury wheat farms. Unpublished report prepared for the New Zealand Fertiliser Manufacturer's Research Association. AgResearch. Hamilton.

Roberts, A.H.C., Morton, J.D., 2009. Fertiliser use on New Zealand dairy farms. New Zealand Fertiliser Manufacturers' Research Association, Auckland, New Zealand. 52 p.

Sparrow, L.A., Salardini, A.A., 1997. Effects of residues of lime and phosphorus fertilizer on cadmium uptake and yield of potatoes and carrots. Journal of Plant Nutrition 20, 1333-1349.

Sparrow, L.A., Salardini, A.A., Bishop, A.C., 1993. Field studies of cadmium in potatoes (*Solanum tuberosum* L.). I. Effects of lime and phosphorus on cv. Russet Burbank. Australian Journal of Agricultural Research 44, 845-853.

Srivastava, P., Singh, B., Angove, M., 2005. Competition adsorption behaviour of heavy metals on kaolinite. Journal of Colloid and Interface Science 290, 28-38

Stafford, A.D., Anderson, C.W.N., Hedley, M.J., McDowell, R.W., 2016. Cadmium accumulation by forage species used in New Zealand livestock grazing systems. Geoderma Regional 7, 11-18.

Tiller, K.G., Gerth, J., Brummer, G., 1984. The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. Geoderma 34, 17-35.

Vasconcelos, I.F., Haack, E.A., Maurice, P.A., Bunker, B.A., 2008. EXAFS analysis of cadmium(II) adsorption to kaolinite. Chemical Geology 249, 237-249.

Welch, R.M., Norvell, W.A., 1999. Mechanisms of cadmium uptake, translocation and deposition in plants. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers Dordrecht, The Netherlands, pp. 125-150.

Williams, C.H., David, D.J., 1977. Some effects of the distribution of cadmium and phosphate in the root zone on the cadmium content of plants. Australian Journal of Soil Research 15, 59-68.

Young, S.D., 2012. Chemistry of heavy metals and metalloids in soils. In: Alloway, B.J. (Ed.), Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Dordrecht, The Netherlands, pp. 51-95.