DISTRIBUTION OF CADMIUM IN LONG-TERM DAIRY SOILS, ITS ACCUMULATION IN SELECTED PLANT SPECIES, AND THE IMPLICATIONS FOR MANAGEMENT AND MITIGATION

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Soil Science

at Massey University, Palmerston North, New Zealand

Aaron David Stafford

2017

ABSTRACT

Accumulation of cadmium (Cd) in agricultural soils, and in pasture, fodder and horticultural crop species is an on-going management concern for New Zealand agriculture. Recent implementation of a new National Cd Management Strategy (MAF, 2011) has increased awareness of this issue. Of key concern are long-term dairy farms in some of NZ's most productive farming districts, where future land-use and trade limitations might be apparent due to their intensive phosphorus (P)-fertiliser application history. The research described in this thesis was undertaken to improve national understanding of; i) soil Cd variability within long-term dairy farms, ii) variability in Cd accumulation between different forage plant species and the consequent risk to livestock grazing these forages, and iii) soil / environmental factors and management / mitigation options that can influence Cd phytoavailability.

Two long-term dairy farms on contrasting soils in the Waikato and Canterbury regions of New Zealand showed wide variability in soil total Cd concentrations (Waikato: 0.48-1.64 mg kg^{-1}, Canterbury: 0.15-0.64 mg kg^{-1}). The strong correlation (R^2 = 0.84-0.85) between soil total Cd and total P concentrations indicated the importance of P fertilisation history on soil Cd variability. However, within blocks of common P fertiliser management history, there was also a strong effect of soil type on soil Cd concentration. Slope class only exerted an influence on soil total Cd concentration when slope exceeded 15°, while application of dairy shed effluent did not appear to have any consistent influence on soil Cd accumulation. All paddocks should be tested independently (based on predominant soil type) to allow Cd-enriched zones to be identified for remediation or alternative management purpose. Individual results can be area-weighted to provide a property-mean soil Cd concentration, where this is required.

For both properties, soil Cd concentrations decreased with depth, however this was effect was stronger and more consistent in the Waikato due to its lack of tillage history. Models

developed from visible and near-infrared reflectance spectroscopy (NIRS) scanning of intact soil cores (collected to 400-600 mm depth) were able to successfully predict soil total carbon (C) (R^2 = 0.91-0.95) and total nitrogen (N) concentrations (R^2 = 0.91-0.92). This technique shows promise for identifying paddock-specific tillage history, and based on the strong correlation between measured soil total Cd and total C and/or total N within each property (R^2 = 0.83-0.90), for identifying Cd distribution within the soil profile. Such information could be used to quantify the tillage depth required to dilute Cd-enriched topsoil to a desired target.

A glasshouse trial on 12 common animal forage species revealed that chicory and plantain accumulated significantly ($P < 0.05$) greater tissue Cd concentrations than other plant species. A subsequent survey of commercial farms across New Zealand validated these findings, with mean tissue Cd concentrations decreasing in the order chicory (1.82 mg kg^{-1} DM) > plantain (0.80 mg kg^{-1} DM) > ryegrass (0.11 mg kg^{-1} DM) > white clover (0.07 mg kg^{-1} DM). A very large range in tissue Cd concentrations for chicory and plantain (0.40-4.50 and 0.23-2.40 mg kg^{-1} DM, respectively) indicating the sensitivity of these species to soil Cd phytoavailability, although only chicory tissue Cd concentration could be satisfactorily explained (R^2 = 0.745) by the variables soil total Cd concentration, pH and total carbon content.

Although soil redox potential is known to influence Cd solubility, a pot trial on two different soils types (Kereone (Allophanic) and Topehaehae (Gley)) revealed that there was no significant difference in 0.05 M $CaCl_2$ soil extractable Cd or plantain tissue Cd concentrations between cyclical flooded (3 days flooded, 11 days drained) and non-flooded (continuously drained) irrigation regimes. However, there was a large difference in soil extractable Cd concentration between the two soils types, with this difference appearing to be driven by differences in soil pH and organic matter content (and possibly clay mineralogy).

Ultra-fine elemental sulphur and hydrated lime soil amendments were used to produce a wide range in soil pH (approximately 5.0-6.5) in two field trials on contrasting soils. There was a

strong negative (linear) correlation (R^2 = 0.64-0.82) between 0.05 M $CaCl_2$ soil extractable Cd concentration and soil pH. Plant tissue Cd concentration was poorly explained by soil pH (chicory R^2 = 0.35-0.52, ryegrass R^2 = 0.19-0.42) and 0.05 M $CaCl_2$ soil extractable Cd concentration (chicory R^2 = 0.11, ryegrass R^2 = 0.28). Perennial ryegrass Cd concentrations remained low (<0.3 mg kg^{-1}) regardless of soil pH, suggesting that animal Cd accumulation risk is low when grazing this plant species, even in Cd-enriched soils at low pH. However, soil pH should be increased to a minimum of 6.5 to decrease livestock dietary Cd exposure when grazing chicory. Mean chicory Cd concentrations were significantly ($P < 0.05$) greater following a period of increased soil moisture, consistent with the increases in Cd solubility observed in the pot trial following soil re-wetting.

This research highlights that Cd accumulation in soil and plants poses a real risk to New Zealand's primary production industries. Existing animal Cd accumulation models indicate that when grazing Cd-accumulating forage species such as chicory and plantain, lamb kidneys may exceed food standard maximum levels in animals much younger than the current meat industry 30-month offal discard age. Understanding Cd accumulation in Cd-sensitive species such as chicory and plantain is important for farmers to be able to manage livestock dietary Cd exposure. Manipulation of soil pH to decrease soil Cd phytoavailability, and utilisation of deep inversion-tillage to bury Cd-enriched topsoil stand out as the most practical management strategies available to farmers. Animal grazing trials on Cd-enriched chicory crops are recommended to evaluate partitioning of ingested Cd, to validate and/or improve the predictions of existing animal Cd accumulation models. Plant breeding opportunities should be a priority focus, to produce chicory / plantain varieties that accumulate lower Cd concentrations in their vegetative tissues.

ACKNOWLEDGEMENTS

There are a number of people who have either directly or indirectly assisted me throughout the course of this study and I take this chance to thank you all. Without your support, this journey would have undoubtedly taken a much more tortuous route!

First of all, thanks to my supervisors at Massey University, Assoc. Prof. Chris Anderson, Prof. Mike Hedley and Dr. Jeya Paramsothy. Your initial positive, proactive response towards my thought of undertaking further study was a massive confidence boost. Thanks for your support to help develop an initial skeleton of an idea into a research proposal, and for providing sound advice and guidance through to its completion. Thanks also to other staff at Massey University who contributed towards this research, notably Dr. Alan Palmer for providing his expertise to the detailed soil surveys carried out within my two case study farms.

My employer Ballance Agri-Nutrients as well as the Fertiliser Association of New Zealand (FANZ) deserve recognition and thanks for supporting this research project, especially given its importance to the fertiliser industry and New Zealand farmers. Without the funding provided by FANZ and the time-allowance provided by Ballance, this project simply would not have been possible. Similarly, I would also like to thank Dr. Roger Hill and Hill Laboratories staff for their analytical support and guidance. Hopefully the knowledge gleaned and new capability created rewards the investments made by these organisations. Significant 'subject matter expert' contributions were made throughout this journey by Prof. Richard McDowell (AgResearch) and Dr. Jo-Anne Cavanagh (Landcare Research), while thanks also goes to Chris Frampton for providing valuable guidance on statistical analysis.

My colleagues at Ballance deserve recognition for their assistance; however as there are too many to name, a generic 'thanks' will have to suffice. In particular, a number of Field Consultants who were quick to assist in providing farmer contacts, and in some cases, helping

me out with some of the more labour-intensive activities such as all-paddock testing and intact soil core sampling.

Lastly, but most importantly, thanks of course to my family who were happy to lend a hand throughout the course of this work. In particular, my wonderful wife Kirsty (who had to take on more than her share of the 'home-duties') and also my father, both of whom assisted me hugely in carrying out all-paddock-testing as well as in establishing / harvesting field trials. Last but not least, thanks to our children Hannah and Liam (the latter whom arrived part-way through this study) for their patience throughout…I know this project distracted me from you guys at times, despite my determination not to let it!

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 : Introduction

New Zealand has a reputation as a clean, safe and reliable food producing nation. Preserving this reputation is important, since as a nation we are heavily dependent on revenue generated from agricultural exports. In the year ended November 2015, dairy, meat and horticultural exports generated approximately $21 billion in revenue, and accounted for approximately 43% of total export earnings (Treasury, 2016).

Global food production is dependent on adequate soil fertility. In their natural state, most New Zealand soils are naturally low in phosphorus (P) (McLaren and Cameron, 1996). As a consequence, regular P fertiliser application has been necessitated to overcome this limitation. As cadmium (Cd) is an unwanted contaminant in P fertiliser (Bolan, 1996; McLaughlin *et al.*, 1996), application of P fertiliser results in incidental Cd inputs and accumulation in agricultural soils (Bramley, 1990; Roberts *et al.*, 1994).

Although Cd accumulation in agricultural soils is a global problem, it has been amplified in New Zealand due to the relatively high P fertiliser demand of intensive ryegrass-white clover pastoral systems. As a consequence, the mean soil Cd concentration of New Zealand agricultural soils is more than double that of non-agricultural soils (0.44 and 0.21 mg kg^{-1} respectively (Roberts *et al.*, 1994)) with a strong influence of soil type and land use history (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b).

As plant Cd accumulation increases with increasing soil Cd phytoavailability (Adriano, 1986) there is concern of increased human dietary Cd exposure as soil Cd continues to accumulate. This is a sensitive issue, since chronic dietary Cd exposure has been linked to several human health disorders, most notably renal tubular dysfunction, which leads to bone demineralisation and weakening (Chaney *et al.*, 1999; Nordberg, 2009; Wallin *et al.*, 2013). Although dietary Cd exposure from food produced in normal, non-polluted agricultural soils is generally considered

low risk (Chaney *et al.*, 1999; Vannoort and Thomson, 2011) public concern over Cd as a soil contaminant still exists, partly since there is still debate as to the sensitivity of human health to chronic dietary Cd exposure (Jarup and Akesson, 2009; Moulis and Thevenod, 2010; Nawrot *et al.*, 2010; Satarug and Moore, 2012). Despite this ongoing debate, there has been recent regulatory movement within the European Union to substantially decrease fertiliser-Cd concentrations to prevent ongoing soil Cd accumulation (EC, 2016).

Cadmium accumulation in soils and food produce is therefore an issue that is extremely relevant to New Zealand agriculture. Ruminant-grazed pastoral systems represent the predominant agricultural land use in New Zealand, accounting for approximately 75% of the total agricultural land area. Although Cd is not found in significant quantities in milk and meat products, Cd accumulates in the liver and kidney of grazing ruminants (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994). To manage this, the New Zealand meat industry currently discards liver and kidney from trade for human consumption for animals greater than 30 months of age (MAF, 2008). Although animal offal accounts for only a small proportion (NZ$211 million, or approximately 3%) of total sheep and beef exports (MIA, 2015), there is potential for collateral damage to other export sales if offal products cannot meet food standard requirements. Furthermore, there is risk to New Zealand's reputation as a safe, environmentally conscientious food producing nation, if Cd accumulation in agricultural soils and produce is not effectively managed.

Because of the importance of agriculture to New Zealand's economy, managing Cd accumulation therefore warrants ongoing investigation. Cadmium accumulation in New Zealand agricultural soils is caused by P fertiliser usage (Bramley, 1990; Roberts *et al.*, 1994; Bolan, 1996; Loganathan *et al.*, 2003). Although the Cd concentration in P fertilisers used in New Zealand has been reduced since the late 1990's (MAF, 2008) in many soils soil Cd enrichment has already occurred because of the unwitting usage of high-Cd South-Pacific P rocks (e.g. Nauru and Christmas Island) for superphosphate manufacture during the 1960's to

early 1990's (Roberts *et al.*, 1994; McLaughlin *et al.*, 1996). Furthermore, our dependence on P fertiliser to drive agricultural productivity means there is risk for ongoing soil Cd accumulation. This challenge is only likely to increase over time, since the future global trade of P rock is expected to be dominated by exports from Morocco and north / west Africa (de Ridder *et al.*, 2012) with these P rock deposits typically containing greater Cd concentrations than many other currently-exploitable alternatives.

To assist in managing ongoing soil Cd accumulation, a Tiered Fertiliser Management System (TFMS) was introduced to New Zealand agriculture in 2011 (MAF, 2011). While in principle the TFMS is a sensible approach to managing soil Cd accumulation, currently there are a number of weaknesses in its approach and to its application. Firstly, soil total Cd concentration alone is not likely to adequately represent risk of Cd accumulation in food produce. This is because many soil-specific factors influence the solubility and phytoavailability of Cd in the soil (Gray *et al.*, 1999d; Loganathan *et al.*, 2012) while there is also large variation in Cd uptake and accumulation between different plant species and cultivars within a species (Gray *et al.*, 2001; Abe *et al.*, 2008; Smolders and Mertens, 2012). Currently, there is a lack of relevant data for many species/cultivars used in modern ruminant-grazed pastoral systems in New Zealand.

Secondly, there is a knowledge gap with regard to the spatial variability of soil Cd within pastoral-grazing systems, particularly long-term dairy farms that have traditionally applied greater annual rates of P fertiliser, and which are therefore likely to have more greatly enriched soil Cd concentrations. This lack of information will make it difficult for practitioners to accurately benchmark a property's soil Cd status within the TFMS, and also to develop practical and cost-effective management strategies where elevated soil Cd concentrations are found to occur. The work in this PhD thesis is designed to help develop the data sets necessary to fill these existing knowledge gaps.

1.1 Research focus

The PhD research project aims to further knowledge with regard to management of Cd in pastoral-grazing systems. The research embodied in this thesis has four main objectives:

1) To evaluate the spatial variability of soil Cd in long-term dairy farming systems with contrasting soils types and management history, using case study farms located in the Waikato and Canterbury regions.
2) To develop plant Cd uptake and accumulation data for various forage species used in modern farming systems, and with modelling, to understand risks of Cd accumulation in the liver and kidney of grazing ruminants.
3) To investigate relationships between soil properties (including total Cd concentration, pH, organic matter content and clay mineralogy) and/or environmental conditions (soil moisture status / redox potential) on soil Cd phytoavailability and plant Cd accumulation.
4) In field trials, to evaluate selected management / mitigation options for Cd-enriched soils.

1.2 Thesis structure

This thesis is composed of nine chapters. Following this introductory chapter, Chapter 2 provides a review of the literature that is relevant to this study. This synthesises knowledge relating to factors that influence soil Cd phytoavailability and plant Cd uptake, as well as the current state of knowledge with regard to Cd in New Zealand agriculture. Chapters 3-8 report on the core research carried out within this PhD project to address the knowledge gaps identified within the literature review. Finally, Chapter 9 summarises the key findings from the research chapters, discusses the implications of this work to Cd management practices in agricultural soils, and also provide recommendations for future research.

CHAPTER 2 : Literature review

2.1 Introduction

Cadmium (Cd) is a naturally occurring non-essential element that can be found in low concentrations in almost all terrestrial and aquatic environments. The average Cd concentration in the Earth's crust is around 0.1 mg kg^{-1}, making Cd the 64th most abundant crustal element (Adriano, 1986). The Cd concentration in different rocks depends on their origin, typically descending in the order sedimentary > metamorphic > igneous rocks (Page and Bingham, 1973). As these rocks provide the parent material for soil development, Cd is also found in our soils, with a global 'natural background' soil Cd range of 0.1-1.0 mg kg^{-1} dry weight (Smolders and Mertens, 2012). Although Cd is naturally present in soil, various anthropogenic soil Cd accumulation factors have been documented. These include land application of industrial wastes, sewage sludge, animal manures and phosphorus (P)-fertiliser, as well as atmospheric deposition near industrial sites (Adriano, 1986).

Accumulation of Cd in the soil is undesirable since Cd is known to be toxic to plants and soil organisms, and accumulation in agricultural soils can result in increased human dietary Cd exposure (McGrath, 1999; Smolders and Mertens, 2012). Elevated dietary Cd intake has been strongly correlated with renal tubular dysfunction, leading to increased bone demineralisation, and increased urinary excretion of calcium and consequent weakening of bone structure (Nordberg, 2009; Wallin *et al.*, 2013). Furthermore, it has been declared that that there is 'sufficient evidence' to include Cd as a known human carcinogen (IARC, 1993) although the linkage between dietary Cd and cancer remains tenuous and uncertain (Chaney *et al.*, 1999; Cho *et al.*, 2013).

Most eco-toxicity research indicates that deleterious impacts on soil biological function occur at soil Cd concentrations greater than that typically associated with agricultural land use (Bollag and Barabasz, 1979; Doelman and Haanstra, 1986; Coppola *et al.*, 1988; Dar and Mishra, 1994; Spurgeon *et al.*, 1994; Dusek, 1995). For example, McGrath (1999) summarised that lowest observable adverse effect concentrations (LOAEC) range from 2-10,000 mg Cd kg^{-1} soil, with tenth percentiles for impacts on soil microbes and processes ranging between 8-20 mg Cd kg^{-1} soil.

In contrast, human dietary Cd intake is relatively sensitive to potential increases brought about by Cd accumulation in agricultural soils. For example, the World Health Organisation (WHO) provisional tolerable monthly intake (PTMI) of 25 mg Cd kg^{-1} bodyweight is only three to seven times the global population-average Cd intake (Smolders and Mertens, 2012). Similarly, the New Zealand Total Diet Study (Vannoort and Thomson, 2011) indicates dietary Cd intake to range between 22% (19-25 year old males) and 46% (5-6 year old children) of the WHO PTMI. However, International debate still exists as to what are appropriate 'tolerable' Cd intakes, resulting from uncertainty regarding dietary interactions that affect Cd absorption and toxicity risks (Chaney *et al.*, 1999) as well as the sensitivity of various chronic human health disorders (including osteoporosis, diabetes and cancer) to dietary Cd intake (Jarup and Akesson, 2009; Moulis and Thevenod, 2010; Nawrot *et al.*, 2010; Satarug and Moore, 2012). The European Food Safety Authority has therefore justified retaining a provisional tolerable weekly intake value of 2.5 mg Cd kg^{-1} bodyweight (i.e. approx. 10 mg Cd kg^{-1} bodyweight $month^{-1}$); a value less than half the WHO PTMI equivalent (Vannoort and Thomson, 2011). Because of this uncertainty, and since dietary Cd intake accounts for more than 90% of the exposure to Cd for the general human population (Smolders and Mertens, 2012), Cd accumulation in agricultural soils remains a sensitive issue that warrants on-going investigation and management.

2.1.1 Why is cadmium a problem for New Zealand agriculture?

Regular P fertiliser application has been necessitated to support intensive agricultural production in New Zealand, since most of our soils are naturally low in P (McLaren and Cameron, 1996). As Cd is a naturally occurring contaminant in the P rocks used to manufacture P fertiliser, Cd accumulation in New Zealand agricultural soils has been linked to P fertiliser usage (Bramley, 1990; Roberts *et al.*, 1994; Bolan, 1996; Loganathan *et al.*, 2003). Traditionally, superphosphate has been the predominant P fertiliser used in New Zealand. Up until the mid-1990's New Zealand superphosphate was commonly manufactured from blends of Cd-rich Nauru and Christmas Island phosphate rock (Bramley, 1990; Loganathan *et al.*, 1995; McLaughlin *et al.*, 1996; Loganathan *et al.*, 2003). As a consequence, the resulting superphosphate was rich in Cd, containing on average around 550 mg Cd kg^{-1} P (Rothbaum *et al.*, 1986; Roberts *et al.*, 1994; McDowell, 2012). At typical rates of 20-40 kg P ha^{-1} y^{-1}, Cd input in P fertiliser applied at that time would have amounted to 11-22 g Cd ha^{-1} y^{-1}. Comparatively, atmospheric deposition has been shown to contribute just 0.09-0.36 g Cd ha^{-1} yr^{-1} to New Zealand agricultural soils (Gray *et al.*, 2003a). Because of the high Cd concentrations in P fertilisers historically used in New Zealand, initial soil Cd research in the early 1990s found that many agricultural soils had Cd concentrations enriched above natural background levels (Roberts *et al.*, 1994).

With awareness of soil Cd accumulation as a long term management issue, the New Zealand fertiliser industry sequentially decreased the Cd concentration in its P fertilisers over the period 1995-1997 to its current maximum Cd concentration of 280 mg Cd kg^{-1} P (MAF, 2008; Rys, 2011). This has led to high Cd phosphate rocks such as Nauru and Christmas Island being largely phased out of superphosphate manufacture. However, the potential for ongoing soil Cd accumulation remains a management challenge for New Zealand agriculture due to our dependence on P fertiliser to drive agricultural production. Left unmanaged, soil Cd accumulation has the potential to increase dietary Cd intake of the New Zealand population

through increased accumulation in locally grown food crops. It also has the potential to jeopardise access to foreign export markets, which represents a serious economic threat given New Zealand's high economic dependence on revenue from agricultural exports.

2.1.1.1 Guideline values for managing soil Cd

In the absence of national standards for Cd in agricultural soils or risk-based critical soil Cd concentrations specific to New Zealand soils (MAF, 2008; Warne, 2011), the New Zealand Water and Wastes Association (NZWWA) guideline for biosolids application (1 mg kg^{-1}, Table 2.1) has often been cited as a reference point for management of soil Cd accumulation, despite this concentration having little scientific basis (Warne, 2011). More recently, a new set of soil contaminant standards (SCS) have been developed to manage risk of human exposure to Cd as part of the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health (NES, Table 2.1).

Table 2.1. Guideline values for management of soil Cd in New Zealand.

		Total Cd (mg kg^{-1})
Soil limit for application of biosolids (NZWWA, 2003)		1.0
National Environmental Standard (NES) Land use scenarios and soil contaminant standards (SCS) for cadmium for protection of human health (adapted from Cavanagh (2012)		
Land use	Comments	SCS (mg kg^{-1})
Rural residential / lifestyle block	25% of produce consumed is assumed to be home grown	0.8 (pH 5.0) 1.4 (pH 5.5) 2.3 (pH 6.0)
Residential	10% of produce consumed is assumed to be home grown	3.0 (pH 5.0) 5.0 (pH 5.5) 7.9 (pH 6.0)
High density residential	No consumption of home-grown vegetables	229
Recreation	Includes playing fields, residential reserves, public green areas and gardens used for passive recreation	400
Commercial / industrial outdoor worker	Based on an outdoor worker who is in contact with surface or near-surface soil	1,300

Although agricultural land is currently exempt from the NES, land use conversion (e.g. agricultural to residential) triggers a requirement for contaminated land assessment (MfE, 2011). At its most stringent, for conversion to rural-residential land use, the SCS is just 0.8 mg kg^{-1}. This is an important consideration, since this SCS lies well within the range of soil Cd concentrations reported for New Zealand agricultural soils (Roberts *et al.*, 1994; Taylor *et al.*,

2007). In some circumstances, remediation of agricultural land would therefore be required before conversion to rural-residential land use could continue. Aside from potentially limiting land use flexibility, association with 'contaminated' land values has potential to negatively influence market perception of New Zealand agricultural food production systems.

2.1.1.2 Tiered Fertiliser Management System

On-going concerns related to the management of soil Cd accumulation arising from P fertiliser use in agricultural land led to formation of the Cadmium Working Group in the mid-2000's. Activity from this group culminated in a new National Cadmium Management Strategy, which was developed with the purpose of "ensuring that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years" (MAF, 2011). Within this strategy, a Tiered Fertiliser Management System (TFMS) was developed as a mechanism to manage the on-going rate of soil Cd accumulation in agricultural land.

The TFMS comprises five soil Cd management tiers separated by four soil total Cd 'trigger' concentrations; 0.6, 1.0, 1.4 and 1.8 mg kg^{-1} (Table 2.2). The basis of the TFMS in managing ongoing soil Cd accumulation is that as soil Cd concentration increases, increasing restrictions on P fertiliser management apply, to the point where no further Cd accumulation is allowed above a soil Cd concentration of 1.8 mg kg^{-1} (MAF, 2011). For farms that have elevated soil Cd concentrations, the TFMS therefore has potential to dramatically affect flexibility in P fertiliser, and potentially, farm management practices. Because of this, the relevance and appropriateness of the soil Cd concentrations used as trigger values within the TFMS is a contentious issue. In the absence of New Zealand-specific risk-based data being available, these trigger values have been derived from a variety of sources including two international soil Cd risk-based values that were hierarchically-prioritised (MAF, 2011).

Table 2.2. Cadmium management tiers and tier boundary trigger values with the TFMS (Cavanagh, 2012).

Tier	Management action required	Cd concentration (mg kg^{-1})	Trigger value (mg kg^{-1})	Source
0	Five-yearly screening soil test for cadmium status	0-0.6	0.6	99th percentile of natural background concentrations
1	Application is restricted to a set of products and application rates to minimise accumulation, and landholders are required to test for cadmium every 5 years using approved programmes	>0.6-1.0	1.0	NZ Biosolids guidelines
2	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.0-1.4	1.4	Canadian soil quality guideline (human and ecological) for agricultural land use
3	Application rates are further managed by use of a cadmium balance programme to ensure that cadmium does not exceed an acceptable threshold within the next 50 years	>1.4-1.8	1.8	UK Soil Guideline value for allotments
4	No further accumulation above the trigger value	>1.8		

Although soil and plant Cd accumulation has been the focus of significant international research, in an international context New Zealand's livestock systems are relatively unique. As a consequence, there is little international data that is relevant to informing Cd management in our pastoral systems. Furthermore, while considerable research was undertaken on Cd in New Zealand agricultural systems during the 1990s, little research has been undertaken since then, despite farm systems evolving considerably. With the rollout of the TFMS, this places greater emphasis on the need to support New Zealand farmers with information that is current and relevant to their farm systems. The aim of this literature review is therefore;

i) To review the current state of knowledge of Cd in New Zealand agricultural systems with respect to land management under the TFMS

ii) To identify gaps in knowledge that could improve our ability to effectively manage soil Cd accumulation and associated risks in agricultural systems.

Within this review, Section 2.2 addresses factors that influence Cd phytoavailability in soils, while Section 2.3 covers factors that influence uptake and expression of Cd in plant tissues. Finally, Section 2.4 synthesises knowledge regarding Cd accumulation in New Zealand agricultural soils, plant species, and grazing livestock.

2.2 Factors affecting soil Cd phytoavailability

In most soils the majority of Cd is found in solid phase (i.e. sorbed to soil exchange surfaces) with only around 1% of the soil total Cd content found in aqueous form (Christensen and Haung, 1999). Of the small amount of Cd found in soil solution, the predominant form is Cd^{2+} with concentrations of other Cd complexes (e.g. sulphate, hydroxyl, carbonate, phosphate) being relatively low (Helmke, 1999; Taylor and Percival, 2001). As summarised in the review of Loganathan *et al.* (2012) precipitation of Cd-complexes is mainly considered to be an issue affecting Cd phytoavailability only in heavily polluted industrial sites, where there is sufficiently high concentration of anions (e.g. carbonates and phosphates) to drive Cd speciation towards insoluble Cd-complexes. At low background Cd concentrations more typical of agricultural soils, Cd sorption-desorption processes are thought to be the most significant soil transformations affecting Cd phytoavailability (Loganathan *et al.*, 2012).

2.2.1 Specific and non-specific sorption of Cd

Like other metal cations in soil solution, Cd^{2+} can adsorb to soil surfaces through either non-specific or specific sorption mechanisms. Non-specific sorption (also known as outersphere adsorption) refers to the electrostatic attraction between the negatively charged cation exchange sites on soil colloids and hydrated metal cations in soil solution (Helmke, 1999). As the metal ion and exchange surface are separated by at least one water molecule, the bond is relatively weak. Hence, non-specifically sorbed cadmium is readily exchangeable and is considered to be highly phytoavailable. Conversely, specific sorption (also known as innersphere adsorption) occurs when the waters of hydration associated with metal ions are partially removed, and as a consequence, a direct covalent bond is formed between the ion and exchange surface (Helmke, 1999). This covalent bond is much stronger than the simple electrostatic attraction that occurs with non-specific sorption. Because of this, Cd that is

specifically sorbed is less easily desorbed to soil solution, and is therefore less phytoavailable than non-specifically sorbed Cd.

2.2.2 Role of clay minerals and organic matter as sorption sites

Clay mineralogy and organic matter content are critical factors influencing Cd sorption behaviour in soils (Loganathan *et al.*, 2012). These characteristics (discussed in Table 2.3) dictate whether a soil possesses predominately permanent or variable negative charge, which governs the soils relative capacity for non-specific versus specific sorption of metal ions.

Variable charge capacity in soils is generated through the exposure of terminal functional groups at the surface of clay minerals (most notably short range order aluminosilicates and iron and aluminium oxides) and soil organic matter. Examples of these terminal functional groups include iron and manganese oxides and oxy-hydroxides exposed at the surfaces of clay minerals, and carboxylic and phenolic groups associated with organic matter (Naidu *et al.*, 1997; Christensen and Haung, 1999). The net negative charge associated with variable charge clays and organic matter is heavily influenced by soil pH, since pH dictates protonation and de-protonation of these terminal functional groups (Naidu *et al.*, 1997; Loganathan *et al.*, 2012). When soil pH is increased this drives de-protonation of surface functional groups, resulting in an increase in the soils net negative charge. Hydrated metal ions (such as Cd^{2+}) can associate with these negatively charged surface groups through simple electrostatic attraction, resulting in non-specific sorption. However, much stronger direct chemical bonds can be established between the negatively charged surface group and the metal cation through the sharing of electron pairs (i.e. covalent bonding) driving specific sorption of the metal ion (Christensen and Haung, 1999; Loganathan *et al.*, 2012). In the case of soil organic matter, the high density and close proximity of surface -OH groups (associated with carboxylic and phenolic groups) is likely responsible for strong specific sorption of Cd^{2+}, through the formation of multidentate bonds that results in metal ion chelation (Young, 2012).

Table 2.3. Summary inorganic and organic sorption surfaces within soil colloids.

Sorption surface	Description and characteristics	References
Layer silicate clays	2:1 layer silicate clays (e.g. smectite, vermiculite) • Terminal functional groups (Al-OH and Si-OH) only occur at the 'broken edges' of clay lattice. These variable charge sites represent only a small proportion of the clay total surface area, hence specific sorption capacity of 2:1 layer silicate clays is low. • Contain predominantly permanent negative charge, arising from isomorphic substitution of structural cations in the lattice structure of layer silicate clays (e.g. Al^{3+} replacing Si^{4+}). • Cd^{2+} is only electrostatically attracted to permanent charge sites, meaning Cd^{2+} sorption is mainly non-specific. 1:1 layer silicate clays (e.g. kaolinite, halloysite) • Contain a greater abundance of variable charge sites, due to exposure of terminal functional groups (Al-OH) along the planer face of the octahedral sheet, as well as at the 'broken edges' of the clay lattice (Al-OH and Si-OH). • As Al-OH groups in particular are known to form strong covalent bonds with metal ions, these 1:1 layer silicate clays have greater specific sorption capacity than 2:1 layer silicate clays.	(Norrish, 1981; McBride, 1989; Havlin *et al.*, 2005; Loganathan *et al.*, 2012)
Short range order (SRO) alumino-silicates	• Examples of SRO aluminosilicates include allophane and imogolite. Allophane is common in well drained soils of volcanic origin. • High variable charge capacity due to the abundance of surface hydroxyl (-OH) groups. • High specific sorption capacity for Cd^{2+}.	(Norrish, 1981; McBride, 1989; McLaren and Cameron, 1996; Christensen and Haung, 1999)
Metal oxides / hydrous oxides	• Al, Mn and Fe hydrous oxides represent variable charge clay minerals with strong specific sorption capacity for metals ions such as Cd^{2+} • The affinity between Cd and O is strong enough to drive off H^{+} ions from metal -OH groups, resulting in a strong covalent bond between Cd^{2+} & the exposed metal oxide. • Deposition of metal oxide coatings on the surface functional groups of layer silicate clays can also create variable charge where originally only permanent charge capacity existed.	(Sposito, 1984; McBride, 1989; Backes *et al.*, 1995; Christensen and Haung, 1999)
Organic matter	• Simple electrostatic attraction exists between hydrated metal cations and the overall net negative charge of humus, generating non-specific sorption of Cd^{2+} • Soft Lewis bases within humus (e.g. sulphur containing organic ligands such as the sulfhydryl groups) have high affinity for Cd^{2+} (as a soft Lewis acid) • High density & close proximity of surface -OH groups (associated with carboxylic & phenolic groups) provides strong specific sorption capacity, through formation of multidentate bonds with metal ions (i.e. chelation)	(McBride, 1989; Christensen and Haung, 1999; Loganathan *et al.*, 2012; Young, 2012)

Few terminal functional groups occur on the planer 'faces' of tetrahedral and octahedral sheets in 2:1 layer silicate clays (e.g. smectite, vermiculite) with terminal functional groups being mainly confined to the end 'edges' of these sheets. In contrast, 1:1 layer silicate clays such as kaolinite tend to have greater variable charge, due to surface hydroxyl groups being exposed along the planer face of the octahedral sheet (Christensen and Haung, 1999; Loganathan *et al.*, 2012; Young, 2012). As the end 'edges' of layer silicate sheets represent only a small proportion of the total surface area of 2:1 layer silicate clays, 2:1 layer silicate clays tend to have low variable charge capacity, with Havlin *et al.* (2005) noting that "*only about 5 to 10% of the negative charge on 2:1 layer silicate clays is pH dependent*". Instead, 2:1 layer silicate clays predominantly possess permanent net negative charge. This permanent net

negative charge is created via isomorphous substitution, whereby a metal ion of lower valence replaces one of higher valence (e.g. Al^{3+} replaces SI^{4+}) within the clay lattice structure (McLaren and Cameron, 1996; Naidu *et al.*, 1997). Since Cd^{2+} is only electrostatically attracted to this permanent negative charge, metal ion sorption to 2:1 layer silicate clays is primarily non-specific.

2.2.3 Factors affecting Cd sorption & desorption

Although clay mineralogy and soil organic matter content dictate the overall soil Cd sorption 'potential', a range of factors influence the availability of these sorption sites, as well as the affinity of Cd ions for these sorption sites. These factors (Table 2.4) include soil pH, the concentration of Cd and other metals in soil / soil solution, the concentration of other cations and/or anions in soil solution, and soil redox potential. Of these, soil pH is generally considered to be the single most important factor regulating heavy metal sorption in soils (Bolan *et al.*, 1999b; Christensen and Haung, 1999; Gray *et al.*, 1999d; Young, 2012).

2.2.3.1 Influence of soil pH

Many researchers (Tiller *et al.*, 1984; Naidu *et al.*, 1994; Srivastava *et al.*, 2005) have shown that sorption of Cd and other heavy metals increases with increasing pH, producing a sigmoid-type curve. This effect is shown in Figure 2.1, whereby a rapid increase in heavy metal sorption occurs over a relatively narrow pH range (generally between pH 4-8); this is referred to as the sorption edge (Loganathan *et al.*, 2012). Within the sorption edge, Cd sorption can increase two to four times per unit increase in soil pH (Christensen and Haung, 1999). In addition to the rapid increase in Cd sorption with increasing soil pH, a decrease in the rate of subsequent desorption has also been observed (Tiller *et al.*, 1984; Gray *et al.*, 1998; Srivastava *et al.*, 2005; Vasconcelos *et al.*, 2008).

Table 2.4. Factors influencing Cd / metal ion sorption and desorption.

Factor	Effect on Cd sorption / desorption	References
Soil pH	• Increasing soil pH neutralises H^+ ions on surface -OH groups associated with organic matter and clay minerals, creating a larger specific-sorption sink for Cd • A rapid increase in Cd sorption occurs within a narrow pH range – this is termed the *sorption edge*. Hypotheses for this effect include: o metal-ion hydrolysis, whereby Cd^{2+} is driven to $CdOH^+$ which has a stronger affinity for sorption sites o Ion-exchange being influenced by change in soil pH, since the net negative charge of variable charge soils increases with increasing pH. o At lower pH, greater H^+ concentration competes with Cd^{2+} for sorption sites o Precipitation of $CdOH^+$ at sorption sites at pH levels below that where hydrolysis of Cd^{2+}in solution would be expected	(Boekhold *et al.*, 1993; Naidu *et al.*, 1994; Bolan *et al.*, 1999a; Bolan *et al.*, 1999b; Bolan *et al.*, 2003c; Loganathan *et al.*, 2012)
Cations in soil solution	• Increased soil solution cationic concentration creates greater competitive ion-exchange interaction, decreasing Cd sorption. • Relative affinity of soil solution cations for soil sorption sites also influences Cd^{2+} sorption. Relative affinity of cations for sorption sites is affected by two key factors; o Valency (e.g. trivalent ions > divalent ions). For example, Cd sorption has been shown to be greater in the presence of Na^+ than Ca^{2+}, at equal ionic strength. o Hydrated radius (ions with smaller hydrated radius have greater affinity)	(Boekhold *et al.*, 1993; Naidu *et al.*, 1994; McLaren and Cameron, 1996; Loganathan *et al.*, 2012)
Anions in soil solution	• Anions in soil solution can influence Cd sorption in two ways : o Formation of Cd-complexes reducing affinity with sorption sites. o Specific sorption of anions to positively charged sites on soil colloids can increase net negative charge of the soil, increasing Cd sorption. • Cd sorption has been found to be higher in the presence of phosphate than sulphate, chloride or nitrate. This was attributed to the specific sorption of phosphate to positively charged sorption sites, increasing the net negative charge of the soil. • High chloride (Cl) concentrations in saline soils drive formation of $CdCl^+$ complexes, reducing Cd affinity for sorption sites & increasing phytoavailability. Fertilisers high in Cl can increase crop Cd accumulation when placed in close proximity to P fertilisers.	(McLaughlin *et al.*, 1994a; Sparrow *et al.*, 1994; McLaughlin *et al.*, 1995; McLaughlin *et al.*, 1996; McLaughlin *et al.*, 1997; Bolan *et al.*, 1999a; Bolan *et al.*, 2003b; Chien *et al.*, 2003; Zhao *et al.*, 2003; Pelletier *et al.*, 2007; Loganathan *et al.*, 2012)
Presence of other metals in solution	• Cd has a lower sorption affinity than most metals, generally following an order related to the stability of metal-complexes: Mercury > Lead > Copper > Zinc > Nickel = Cobalt > Cadmium • Preferential binding of higher affinity metal ions is likely to reduce the availability of specific sorption sites available to bind with lower affinity metals such as Cd. • Zinc (Zn) is considered influential in Cd sorption, since Zn & Cd are very similar in terms of basic elemental characteristics, sorption/desorption behaviour, and since Zn concentration in soil is much higher than Cd • Metal interactions are unlikely to be relevant to uncontaminated agricultural soils	(Tiller *et al.*, 1984; Adriano, 1986; Christensen and Haung, 1999; Srivastava *et al.*, 2005; Kim *et al.*, 2009; Serrano *et al.*, 2009; Loganathan *et al.*, 2012; Young, 2012)
Soil redox potential	• Soil redox potential can influence metal-ion solubility through various mechanisms: o Dissolution of manganese (Mn) and iron (Fe) hydrous oxides under weak- to moderately-reducing conditions can release co-sorbed metal ions. This is known to influence phytoavailability of some metals, notably cobalt and arsenic. o Formation of insoluble metal-sulphide complexes can occur under prolonged, strongly reducing soil conditions. For example, this has been attributed to decreased Cd availability that occurs during the flooded phase of rice cultivation. o Changes in soil pH can occur through consumption of H^+ during reducing phases & generation of H^+ during oxidising phases. Upon saturation, soil pH reaches a minimum within a few days, before increasing to stabilise at near-neutral pH. Change in soil pH can directly influence metal sorption behaviour & specific sorption capacity.	(Gotoh and Patrick, 1972; Ponnamperuma, 1972; Gotoh and Patrick, 1974; Masscheleyn *et al.*, 1991; Atta *et al.*, 1996; Charlatchka and Cambier, 2000; Kashem and Singh, 2001; DeLaune and Reddy, 2005; Cornu *et al.*, 2009; de Livera *et al.*, 2011; Young, 2012; Zhang *et al.*, 2012; Bhatti *et al.*, 2013; Zheng *et al.*, 2013; Hindersmann and Mansfeldt, 2014; Sparrow and Uren, 2014)

This is likely to be related to the increase in variable charge as soil pH increases, resulting in an increase in the proportion of irreversibly bound Cd^{2+} associated with specific sorption sites (Tiller, 1989), and potentially increased formation of $CdOH^+$ species that have higher absorption affinity than Cd^{2+} (Naidu *et al.*, 1994; Bolan *et al.*, 2003c). As the energy required to

break the covalent bonds associated with specific sorption is likely to be greater than the energy required to establish them (McBride, 1989), this may explain why desorption of specifically sorbed Cd occurs at a slower rate than the initial sorption.

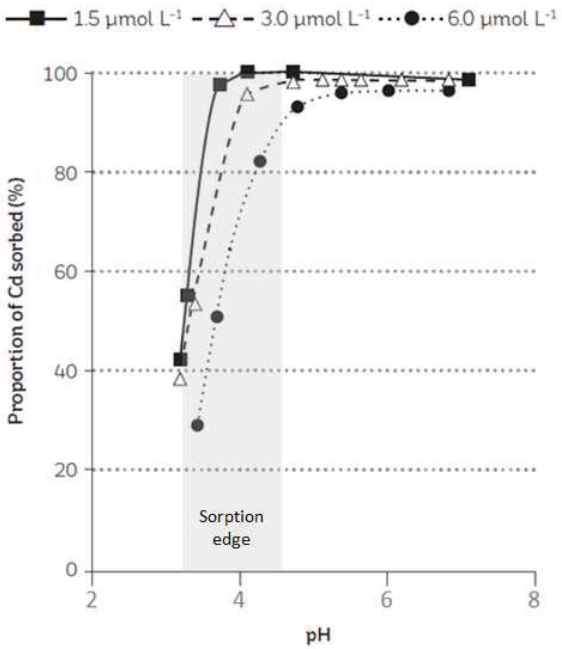

Figure 2.1. Effect of pH and soil solution Cd concentration on sorption of Cd to a New Zealand Allophanic soil (redrawn and adapted from Naidu *et al.* (1994)).

The effect of soil solution Cd concentration on Cd sorption and the shape of the sorption edge is also shown in Figure 2.1. At equivalent pH values, the proportion of added cadmium sorbed decreases as soil solution Cd concentration increases. This is likely due to specific sorption sites becoming saturated, and since displacement of other cations by Cd also creates greater competition for the remaining sorption sites. This effect is stronger at lower pH values (Figure 2.1) due to the decrease in overall specific sorption capacity.

2.2.3.1.1 Liming to reduce soil Cd phytoavailability

Because of the over-riding effect of soil pH on Cd sorption capacity in variable charge soils, liming of acid soils is generally recognised as being the most practical and cost effective means to reduce solubility and phytoavailability of Cd and other heavy metals (Young, 2012). Liming

to maintain soil pH at the upper end of the desired agronomic optimum range is advocated as a management solution to reduce the potential for plants to accumulate Cd from high Cd soils (FANZ, 2016). However, despite many pot trials showing a strong decrease in plant Cd concentrations with increasing pH (Maier *et al.*, 1997; Gray *et al.*, 1999c; Maier *et al.*, 2002) several authors have reported inconsistent effects from liming in field trials, with decreases, increases and no-effect on plant Cd concentrations all being reported in the literature (Andersson and Siman, 1991; Sparrow *et al.*, 1993a; Li *et al.*, 1996; Oliver *et al.*, 1996; Maier *et al.*, 1997; Maier *et al.*, 2002). This variability in the efficacy of lime to reduce plant tissue Cd concentration may be attributable to differences in application timing or soil mixing employed in different studies (Sparrow and Salardini, 1997). Numerous studies have shown that when lime is broadcast on the soil surface, peak effects on topsoil (0-75 mm) pH often occur at least a year after lime application, while the influence on pH deeper down the soil profile is small and takes much longer to occur (Wheeler, 1997; Morton *et al.*, 1998b; Wheeler and O'Connor, 1998; Morton *et al.*, 2005; Flower and Crabtree, 2011; Moir and Moot, 2014).

2.2.3.2 Influence of soil redox

Numerous studies (Kashem and Singh, 2001; Cornu *et al.*, 2007; de Livera *et al.*, 2011; Zhang *et al.*, 2012; Zheng *et al.*, 2013; Hindersmann and Mansfeldt, 2014) have shown that change in soil redox potential (driven by change in soil moisture content) can influence soil Cd solubility and phytoavailability (Table 2.4). As soil redox potential can influence soil pH through the consumption or generation of protons during reductive or oxidative processes, respectively (Ponnamperuma, 1972; Narteh and Sahrawat, 1999; Charlatchka and Cambier, 2000; Young, 2012), many authors have shown consequent impacts on metal solubility due to the overriding effect pH has on metal sorption (Iu *et al.*, 1981; Atta *et al.*, 1996; Charlatchka and Cambier, 2000; Kashem and Singh, 2001; Hernandez-Soriano and Jimenez-Lopez, 2012). Furthermore, under weakly- and moderately-reducing soil conditions (defined by approximate *Eh* ranges of 400 to 200 mV, and 200 to -100 mV, respectively) dissolution of manganese (Mn) and iron (Fe)

hydrous oxides can occur, respectively, as a result of Mn^{4+} and Fe^{3+} being reduced to their more soluble Mn^{2+} and Fe^{2+} oxidation states (McLaren and Cameron, 1996; DeLaune and Reddy, 2005; Young, 2012; Hindersmann and Mansfeldt, 2014). Numerous studies have shown consequent increases in the solubility and phytoavailability of metals (including Cd) affiliated with these Mn/ Fe hydrous oxides (Atta *et al.*, 1996; Cornu *et al.*, 2009; Bhatti *et al.*, 2013; Hindersmann and Mansfeldt, 2014; Sparrow and Uren, 2014). Lastly, formation of insoluble Cd-sulphide complexes under prolonged anaerobic, strongly-reducing conditions (*Eh* values <100 mV) can also reduce Cd solubility (Cornu *et al.*, 2007; de Livera *et al.*, 2011; Zhang *et al.*, 2012; Zheng *et al.*, 2013; Hindersmann and Mansfeldt, 2014).

Most international research into the effect of soil redox potential on Cd solubility / phytoavailability appears to have focussed on extreme or prolonged reducing conditions (e.g. under rice paddies), conditions which are not relevant to New Zealand agricultural soils. The influence of infrequent, short-period saturation and/or fluctuating soil moisture, which is more relevant to New Zealand agricultural soils, does not appear to be well understood.

2.3 Factors affecting plant Cd uptake and accumulation

While Cd is considered a non-essential element, it is readily taken up by plants. Below phytotoxic concentrations, plants generally appear to have little ability to regulate Cd uptake (Adriano, 1986). Hence, as soil Cd phytoavailability increases so too does plant Cd accumulation, with some studies showing a near linear relationship (Williams and David, 1977; Adriano, 1986). However, variation exists in regard to relative Cd accumulation in different plant tissues. For example, Cd concentration tends to be greater in older plant leaves relative to young, indicating limited Cd remobilisation once deposited (Page and Feller, 2005). Furthermore, the concentration of Cd in plant roots may exceed that of the surrounding soil, while Cd concentrations in roots tend to be greater than in above-ground vegetative tissues

(i.e. stem and leaf), which in turn tend to be greater than in reproductive tissues (i.e. grains, seeds and fruit) and tubers (Bingham *et al.*, 1975; Adriano, 1986; Dunbar *et al.*, 2003).

As a general rule, monocotyledonous species (e.g. wheat, ryegrass and rice) tend to accumulate lower tissue Cd concentrations than dicotyledonous species (e.g. brassicas, potatoes, clover) (Bingham *et al.*, 1975). However, large variation in Cd uptake and accumulation has been reported between species (Adriano, 1986; Roberts *et al.*, 1994; Gray *et al.*, 1999a, c) as well as between cultivars within a species (Florijn and Van Beusichem, 1993; McLaughlin *et al.*, 1994b; McLaughlin *et al.*, 1997; Gray *et al.*, 2001; Dunbar *et al.*, 2003; Gray and McLaren, 2005; Abe *et al.*, 2008). This inter- and intra-species variation in Cd accumulation is likely to be driven by differences in root absorption and internal metal transfer efficiencies, as well as variation in plant tolerance to Cd toxicity (Adriano, 1986; Florijn and Van Beusichem, 1993; Dunbar *et al.*, 2003).

2.3.1 Transport of Cd from soil solution across the root membrane

Most research on plant uptake of Cd has focussed on the absorption of Cd^{2+}. Although Cd-chloride complexes are also highly phytoavailable and are an important contributor to plant Cd uptake in saline soils (McLaughlin *et al.*, 1994a; McLaughlin *et al.*, 1997) Cd^{2+} is likely to be the main Cd species in New Zealand agricultural soils that are uncontaminated by chloride (Taylor and Percival, 2001). Reviewing Cd uptake mechanisms in plants, Welch and Norvell (1999) note that at low solution Cd^{2+} concentrations most relevant for agricultural soils, absorption and entry of Cd^{2+} across the root membrane becomes saturated and most likely limited by the availability of divalent metal transporter proteins. This is an important factor that may explain why plant tissue Cd concentrations may be 'diluted' as plant growth rates increase (discussed in Section 2.3.3).

Increased Cd accumulation has been observed in plants deficient in Zn (Oliver *et al.*, 1994; McLaughlin *et al.*, 1995). It has been hypothesised that this is related to a loss in root

membrane integrity, given that Zn is known to play a key role in maintaining membrane integrity (Welch and Shuman, 1995). Impaired root membrane integrity due to Zn deficiency has been linked with abnormally high accumulation of phosphorus, iron and manganese in plant tissue (Welch and Norvell, 1999). Correcting Zn deficiency usually results in a decrease in Cd uptake and accumulation. However, research has also shown that further increases in Zn availability can actually increase Cd accumulation, possibly due to the greater affinity of Zn^{2+} for soil sorption sites resulting in increased Cd^{2+} desorption, or through yield reductions induced through Zn-toxicity (Smilde *et al.*, 1992; Welch and Norvell, 1999). Zinc deficiency in New Zealand agricultural soils is extremely rare (McLaren and Cameron, 1996) suggesting application of Zn will have little role in managing plant Cd accumulation. However, in Australian research on potatoes, McLaughlin *et al.* (1995) reported that at four out of five sites deemed to have adequate Zn nutrition, Zn application (5-10 kg Zn ha^{-1}) decreased Cd concentrations in potato tubers by 10-33%. This inconsistency suggests that our understanding of the interaction between Zn and Cd on plant Cd uptake and accumulation is incomplete.

It has also been hypothesised that increased 'incidental' uptake of Cd could result from plant adaptive-response mechanisms that are triggered to sequester greater amounts of a deficient essential metal (e.g. zinc, copper, iron, manganese) from the soil (Welch and Shuman, 1995; McLaughlin *et al.*, 1996; Welch and Norvell, 1999). These possible plant adaptive-response mechanisms include:

- Increased secretion of H^+ and organic acids from roots to acidify the soil surrounding the roots and decrease specific sorption of metal ions,
- Increased secretion of reductases from the root system to reduce metal-oxide complexes in the soil and increase metal-ion availability,
- Increased activity of micronutrient transport proteins within the root membrane,
- Morphological adaption of the root system, with increased formation of fine root hairs.

As a key example, the amino acid phytometallophore is known to be excreted from the roots of cereals for the purpose of chelating various essential metals. In addition to increasing metal availability, metal adsorption rates are thought to increase via access to specific phytometallophore-metal binding and transport sites that exist within plant root membranes (Welch and Shuman, 1995; Welch and Norvell, 1999). It has been postulated that increased incidental plant Cd uptake could result from chelation and absorption mechanism associated with phytometallophore secretion. However, similar to Zn, plant deficiencies for essential cationic trace elements (e.g. iron, copper, manganese) are rare in most New Zealand agricultural soils (McLaren and Cameron, 1996), marginalising the importance of this mechanism in plant Cd accumulation.

2.3.2 Translocation from the root to other plant tissues

Although studies have shown high Cd mobility via the phloem network, xylem-mediated root-to-shoot Cd translocation efficiency is highly variable between plant species and cultivars within a species (Dunbar *et al.*, 2003; Reid *et al.*, 2003; Tanaka *et al.*, 2007). For these reasons, root-to-shoot Cd translocation efficiency is considered to be a key factor regulating expression of Cd in above-ground plant tissues and driving variation between different plant species and cultivars (Welch and Norvell, 1999). Supporting this, Uraguchi *et al.* (2009) found that there was little difference in root tissue Cd concentrations between various rice cultivars classified as either high or low grain Cd accumulators. However, there was a strong correlation between Cd concentration in the xylem sap and that found in shoot and grain tissue, indicating the critical influence of Cd remobilisation/translocation efficiency from root tissues. Similarly, Florijn and Van Beusichem (1993) reported similar total plant Cd uptake for different maize breeding lines, however internal distribution varied greatly due to large differences in translocation efficiency from root to shoot tissues.

2.3.2.1 Cadmium accumulation in vegetative tissues - shoot Cd 'excluders' versus 'translocators'

Plant species and cultivars can be grouped into two classes based on whether they are shoot Cd 'excluders' or active shoot Cd 'translocators' (Smolders and Mertens, 2012). Shoot Cd excluders are characterised by shoot to root Cd concentration ratios less than 0.05. These plants have limited ability to translocate Cd from root tissues, possibly serving as a mechanism to manage Cd toxicity (Grant *et al.*, 1999). Species within the Leguminosae family (e.g. peas, beans, clover, lucerne) and Gramineae family (e.g. maize, wheat, barley, ryegrass) tend to be shoot Cd 'excluders'.

In contrast, shoot Cd 'translocators' have a much greater capacity for internal Cd translocation, meaning Cd is more efficiently mobilised from the root and transported to other plant tissues via the xylem network. Shoot Cd 'translocators' are characterised by shoot to root Cd concentration ratios greater than 0.25 (Smolders and Mertens, 2012). Plant species within the families Solanaceae (e.g. potato, tomato), Asteraceae (e.g. lettuce, sunflower, chicory) and Brassicaceae (e.g. cabbage, broccoli, turnip, radish) tend to be shoot Cd 'translocators', consequently containing greater Cd concentrations in vegetative tissue. Placement of plant species into shoot Cd 'translocator' or 'excluder' groupings is a broad generalisation, since large variation also exists between different cultivars within a species. Again, citing the maize genotype study of Florijn and Van Beusichem (1993) although the majority of maize genotypes had shoot to root Cd ratios less than 0.05 ('excluders'), some genotypes had shoot to root Cd ratios of around 0.7 ('translocators').

Metal hyperaccumulating plant species are capable of accumulating vegetative tissue metal concentrations 50-500 times greater than that in the soil (Chatterjee *et al.*, 2013). Such plant species may offer potential for phyto-remediation of metal contaminated soils. Although most hyperaccumulator species that have been identified are specific to nickel (Chatterjee *et al.*, 2013), some Cd hyperaccumulators have also been identified, including *Thlaspi caerulescens*

(Liu et al., 2008), *Sedum alfredii* (Yang *et al.*, 2014) and *Solanum nigrum* (Wei *et al.*, 2013). Consistent with their classification as shoot Cd 'translocators', the Asteraceae and Brassicaceae families are listed as containing an unusually high proportion of metal hyperaccumulating species (Gupta, 2013). Unfortunately, many potential hyperaccumulators are limited by low growth rate / biomass characteristics and limited habitat versatility (Chaney *et al.*, 2005), although there may be opportunity through genetic manipulation to increase Cd accumulation in non-hyperaccumulating species that have more favourable growth characteristics (Chatterjee *et al.*, 2013).

2.3.3 Effect of plant growth rate / yield on tissue Cd concentration

A common theme of the literature is that plant tissue Cd concentration is inversely related to plant growth rate or yield (Williams and David, 1973, 1977; Andersson and Hahlin, 1981; Mortvedt *et al.*, 1981; Mortvedt, 1987; Smilde *et al.*, 1992; Gray *et al.*, 1999c). For example, in a long-term soil fertility trial site run in the USA, Mortvedt (1987) reported that plant tissue Cd concentrations were greater in control plots than in areas treated with farm yard manure (FYM) or P fertiliser, despite these plots having significantly greater soil Cd. The lower plant tissue Cd concentrations in this case were attributed to the much higher plant yields in the FYM / P fertiliser plots.

However, it is possible that this inverse relationship between yield and tissue Cd concentration is also influenced by other factors such as overall Cd phytoavailability, and differences between plant species / cultivars to absorb Cd from the soil and transfer it to above ground tissues. For example, again citing the research of Mortvedt (1987) Cd in wheat straw was diluted relative to control plants when yield was increased using low-Cd (8.6 mg Cd kg^{-1} P) P fertiliser. However, when high-Cd (366 & 757 mg Cd kg^{-1} P) P fertiliser was applied, the increase in yield was offset by increased Cd uptake, such that Cd concentrations in these treatments were similar to the control plants. This result suggests that with increased growth

rate, Cd uptake by the plant root and internal re-mobilisation / translocation did not limit Cd accumulation in the straw. Instead, it implies that at low soil Cd phytoavailability, desorption of Cd from solid phase may not be sufficiently rapid enough to 'recharge' Cd in soil solution as it is taken up by the plant root. It is possible than that factors regulating Cd solubility and Cd sorption/desorption dynamics (total Cd, soil pH, organic matter content, clay mineralogy etc.) may influence whether an inverse relationship exists between yield / growth rate and tissue Cd concentration.

2.4 Cadmium in New Zealand agriculture

The need to develop robust, New Zealand-specific data to enable more accurate assessment of Cd-related risks to food safety and trade was first cited by Bramley (1990). Following this, a number of studies were initiated to quantify Cd in New Zealand agricultural soils, plants and livestock. Knowledge from these studies that is pertinent to the application of the TFMS and agricultural Cd risk management is reviewed in this section.

2.4.1 Cadmium in New Zealand agricultural soils

2.4.1.1 Soil Cd by soil type, region and land use

Table 2.5 summarises the findings of three key studies (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b), which provide an overview of the range and variability in national soil Cd concentrations with respect to soil type, land use and region. These studies show that soil Cd enrichment has occurred in many New Zealand agricultural soils, although soil Cd concentrations in New Zealand are similar to those reported internationally (Table 2.6).

Table 2.5 indicates that soil Cd concentrations in New Zealand agricultural soils are likely to be highest where there is a combination of:

i. A long history of intensive land use (intensive land use requires greater P fertiliser inputs to maintain productive capacity)

ii. Soils with low natural P fertility and strong P buffering capacity (requiring greater P fertiliser inputs to lift P fertility to a desired 'optimum' level)

iii. Soils with high specific sorption capacity for Cd.

Table 2.5. Summary of studies investigating soil Cd concentrations in New Zealand soils.

Roberts *et al.* (1994)	• 312 pastoral farming sites (P fertilised) and 86 'native' sites (non-P fertilised), using 0-75 mm sampling depth. • Mean soil Cd conc. for native and pastoral sites was 0.20 and 0.44 mg kg^{-1}, respectively • Range in soil Cd conc. for native sites was 0.02-0.77 mg kg^{-1}, and for pastoral sites 0.04-1.53 mg kg^{-1} • Under pastoral land use, significant enrichment of soil Cd levels occurred in 6 out of 8 soil groups • Mean soil Cd conc. was highest in Yellow Brown Pumice, Yellow Brown Loam and Peat soil groups (corresponding to Pumice, Allophanic and Organic Soil Orders) at 0.75, 0.70 and 0.69 mg kg^{-1}, respectively. • Soil Cd conc. was strongly correlated to total-P concentration, indicating a correlation with P fertiliser use.
Taylor *et al.* (2007)	• Based on 1794 samples (mainly 75 & 100 mm depth) collected over two main periods (1989-1995 and 2000-2006). Includes the data of Roberts *et al.* (1994). • The mean soil Cd conc. for undisturbed (non-P fertilised) sites was 0.16 mg kg^{-1}, versus 0.35 mg kg^{-1} for all sites. • Range in soil Cd conc. across all sites was 0 (not detected) - 2.52 mg kg^{-1} • By land use, mean soil Cd conc. descending in the order: dairying (0.73 mg kg^{-1}) > kiwifruit (0.71 mg kg^{-1}) > berries (0.68 mg kg^{-1}) > orchards (0.66 mg kg^{-1}) > market gardening (0.46 mg kg^{-1}) > drystock pasture (0.40 mg kg^{-1}). Cropping soils were generally below the national average of 0.35 mg kg^{-1}. • Greatest mean soil Cd conc. in Taranaki, Waikato & Bay of Plenty regions (0.69, 0.55 & 0.53 mg kg^{-1}, respectively).
Cavanagh (2014b)	• Survey comprised of 3917 sampling locations (mainly commercial farms) collected by the fertiliser industry post-2006 (mixed sampling depths of 0-75 mm & 0-150 mm). • National median & mean Cd conc. of 0.32 & 0.44 mg kg^{-1}, respectively (range 0-2.14 mg kg^{-1}). • Highest median Cd conc. in Waikato, Taranaki & Bay of Plenty regions (0.74, 0.71 & 0.54 mg kg^{-1}, respectively). • By land use, mean soil Cd conc. descending in the order: dairying (0.59 mg kg^{-1}) > orchard (0.55 mg kg^{-1}) > drystock (0.33 mg kg^{-1}) > arable (0.28 mg kg^{-1}) > non-agricultural (0.13 mg kg^{-1}). • Volcanic and peat soils had the highest median soil Cd concentration (both approx. 0.75 mg kg^{-1}), followed by pumice soils (approx. 0.5 mg kg^{-1}) with sedimentary soils being the lowest (approx.. 0.25 mg kg^{-1}). • No clear trend in Cd conc. over time (though limited by inconsistency in sampling sites over time).

Table 2.6. Summary of soil Cd concentrations reported internationally**.**

Country	Soil	No. of samples	Sampling depth (mm)	Cd mean (mg kg^{-1})	Cd range (mg kg^{-1})	Source
Sweden	Agricultural	361	0-200	0.22	0.03-2.30	Roberts *et al.* (1994)
Denmark	Agricultural	44	0-200	0.25	0.03-0.90	
Netherlands	Agricultural	925	0-200	0.40	0.21-0.59*	
Australia	Agricultural	9	0-100	0.13	0.03-0.32	
England & Wales	Rural	2776	0-150	1.20	0.01-4.10	
Canada	Agricultural	296	0-150	0.56	0.10-8.10	
United States	Agricultural	3045	0-200	0.13	0.03-0.32	
Netherlands	Hort. & agricultural	708	Mostly 0-200	0.5	0.04-14	Wiersma *et al.* (1986)
Australia	Dairy pasture	120	0-100	0.56	0.01-13.9	McLaughlin *et al.* (1996)
United Kingdom	Rural	51	0-150	0.83	**	Weeks *et al.* (2007)
Europe	Agricultural	840	***	0.284	90% less than 0.48	Smolders (2013)

*Standard deviation – range of values not available
**Not available
***Not specified

Based on the data in Table 2.5, long-term dairy and horticultural (orchard) land use on Allophanic, Pumice and Organic Soil Orders in the Waikato, Bay of Plenty and Taranaki regions are likely to have the most enriched soil Cd status, and are therefore likely to attract the most

scrutiny under the TFMS. Consistent with this, Taylor *et al.* (2007) identified that all soil Cd concentrations exceeding 1.0 mg kg^{-1} were sourced from the Waikato, Taranaki and Bay of Plenty regions, while Kim (2005) estimated that 11% of pastoral and 17% of horticultural soils in the Waikato exceeded a soil Cd value of 1.0 mg kg^{-1}. The effect of land use intensity and P fertiliser application history on soil Cd enrichment was further reinforced by McDowell *et al.* (2013). Using soil Cd and P data from 'minimally disturbed' sites, McDowell *et al.* (2013) determined that by land use, anthropogenically-derived Cd as a proportion of soil total Cd descended in the order dairy > horticulture > drystock > forestry > arable.

2.4.1.2 Cadmium accumulation rates

Various New Zealand studies have quantified the rate of soil Cd accumulation as influenced by P fertiliser application rate and land management history (Table 2.7).

Table 2.7. Examples of New Zealand studies that have quantified Cd accumulation rates in New Zealand soils.

Reference	Details	Findings
Loganathan *et al.* (1995)	Data from the Ballantrae long-term hill country fertiliser trial site (Manawatu) that had received ~38 kg P ha^{-1} yr^{-1} as single superphosphate (SSP) for 20 years	• Mean soil Cd accumulation rate of 0.015 mg kg^{-1} yr^{-1} (to 30 mm depth)
Taylor (1997)	Comparison of soil sample results from the same sampling locations at 2 points in time (30-50 years apart). P fertiliser application rates not specified for the range of sites.	• Mean soil Cd accumulation rate of 0.01 mg kg^{-1} yr^{-1} (mainly 0-150 mm samples)
Zanders *et al.* (1999)	Waikato drystock farm receiving on average ~11 kg P ha^{-1} yr^{-1} as SSP	• Mean soil Cd accumulation rate of 0.01 mg kg^{-1} yr^{-1} (to 75 mm depth)
Schipper *et al.* (2011)	Whatawhata long-term hill country trial (Waikato). P fertiliser applied to farmlets at 0, 30, 50 & 100 kg ha^{-1} yr^{-1}, as SSP between 1983-1988 & as triple superphosphate (TSP) post-1988. Cd in the SSP and TSP was approximately 320 and 175 mg Cd kg^{-1} P, respectively.	• Over 1983-1988, the mean soil Cd accumulation rate at 50 and 100 kg P ha^{-1} yr^{-1} was 0.032 and 0.040 mg kg^{-1} yr^{-1} (averaging 'easy' & 'steep' slopes, samples to 75 mm depth). No significant increase in soil Cd at 30 kg P ha^{-1} yr^{-1}. • Since 1989, only 100 kg P ha^{-1} yr^{-1} on 'easy' slopes showed a significant increase in soil Cd, equal to 0.015 mg kg^{-1} yr^{-1}. At lower P fertiliser rates no significant increase in soil Cd occurred, likely due to lower Cd concentration of TSP
McDowell (2012)	Data from the Winchmore border dyke-irrigated long-term fertiliser trial (Canterbury). SSP applied at two rates (~17 and ~34 kg P ha^{-1} yr^{-1}) since 1952.	• Mean soil Cd accumulation rates of 0.003 and 0.005 mg kg^{-1} yr^{-1}, for 17 & 34 kg P ha^{-1} yr^{-1}, respectively (75 mm samples). • Modelling & soil test data indicate most of this increase occurred up until 1990, with soil Cd levels stable since.

These studies show that prior to the reduction in the maximum Cd concentration in P fertilisers used in New Zealand in the mid 1990's, historic soil Cd accumulation rates have been in the order of 0.003-0.04 mg kg^{-1} y^{-1}, depending on rate of P fertiliser and depth of soil

sampling. Recent research has suggested that since the mid-1990s there has been a plateau in soil Cd concentration data with little increase in soil Cd concentration detectable since this time (Schipper *et al.*, 2011; McDowell, 2012). Although limited to just two studies, this coincides with the reduction in maximum P fertiliser Cd concentration that occurred between 1995-97 (MAF, 2008; Rys, 2011), and is supported by soil Cd survey data (Cavanagh, 2014b) that shows no clear trend in soil Cd concentrations post-2006.

2.4.1.3 Cadmium distribution with soil depth

Under non-cultivated pastoral conditions, soil Cd has been shown to be non-uniformly distributed in the soil profile, with Cd concentrations decreasing with increasing soil depth (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999). This is exemplified in Figure 2.2.a, which describes Cd distribution with depth in a well fertilised, hill-country allophanic soil under long-term pastoral land use. Accumulation of Cd near the soil surface is likely related to the concentration of organic matter within the topsoil layer, which provides specific-sorption capacity for Cd (McBride, 1989). In addition, soil Cd extracted from depth by plant roots will be returned to the soil surface via recycled animal dung (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) and plant detritus.

In contrast, where regular soil tillage has occurred, soil Cd concentrations are likely to be more homogeneous with depth. Roberts *et al.* (1995) reported that in soils regularly cultivated for vegetable and cereal cropping, soil Cd concentrations did not decrease substantively with increasing soil depth, with Cd concentrations at 0-200 mm depth representing 83-100% of that at 0-50 mm depth. This is supported by research that has modelled soil Cd redistribution with long-term cultivation, which indicated that soil Cd becomes homogenously mixed within the 200 mm plough layer, with minimal Cd movement deeper into the soil profile beyond the cultivation layer (Chen *et al.*, 2009).

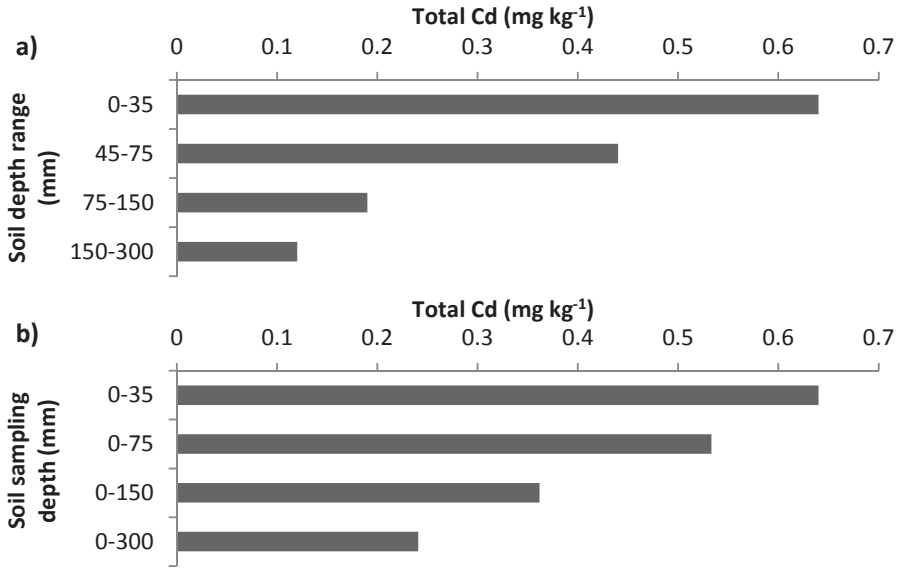

Figure 2.2.a) Variation in soil total Cd concentration with soil depth, and **b)** the effect of soil sampling depth on total soil total Cd concentration in an allophanic, P fertilised hill-country pasture soil (adapted from Zanders *et al.* (1999)).

Because of the non-uniform depth distribution of Cd under permanent pasture, soil sampling depth can have a large influence on Cd concentrations determined. This is indicated in Figure 2.2.b, where soil Cd weighted over the 0-75 mm depth range (0.53 mg kg^{-1}) represents approximately 83% of that over the 0-35 mm depth range (0.64 mg kg^{-1}). Cadmium concentrations decrease markedly below 75 mm soil depth, meaning that soil Cd concentration assessed at a sampling depth of 0-150 mm (0.36 mg kg^{-1}) represents only 68% of that at 0-75 mm. Standard soil fertility assessment depth for New Zealand pastoral systems is 0-75 mm (Roberts and Morton, 2009) whereas horticulture / arable farms use 0-150 mm samples. To provide consistency across different land uses, the New Zealand Fertiliser Industry has recommended standardising 0-150 mm as the 'definitive' soil Cd assessment depth under the TFMS (FANZ, 2016).

2.4.1.3.1 Cadmium leaching

Under non-cultivated conditions, the observed accumulation of Cd near the soil surface infers that Cd has limited mobility in the soil. This inference is supported by Cd leaching data from

several New Zealand studies. Gray *et al.* (2003b) reported annual Cd leaching losses from six New Zealand agricultural soils to range between 0.27-0.86 g ha^{-1} y^{-1} (Table 2.8) which the authors noted would be equivalent to around 5-15% of the Cd in single superphosphate applied at 200 kg ha^{-1} y^{-1} (based on 280 mg Cd kg^{-1} P in the superphosphate). Similarly, Loganathan and Hedley (1997) reported Cd leaching below 200 mm depth to account for less than 5% of the Cd applied in ten years of annual P fertiliser inputs, with 90% of the Cd that was applied being recovered in the top 120 mm of the soil profile.

Table 2.8. Cadmium leaching and variation in soil Cd concentration with depth for six New Zealand pastoral agricultural soils (adapted from Gray *et al.* (2003b)).

Soil (0-250 mm depth)	Total Cd (mg kg^{-1})	pH	Total C (%)	CEC ($cmol_c$ kg^{-1})	Cd leached (g ha^{-1} y^{-1})
Orthic Pumice-1	0.44	5.3	10.6	9.5	0.35
Orthic Allophanic-1	0.53	4.9	12.3	6.6	0.86
Orthic Allophanic-2	0.52	5.4	6.6	7.2	0.43
Orthic Pumice-2	0.69	5.3	4.6	4.6	0.28
Brown	0.41	5.6	6.4	13.8	0.54
Immature Pallic	0.19	5.9	3.3	17.2	0.27

The amount of Cd in soil solution that is susceptible to leaching / translocation in the soil profile is likely to be influenced by soil-specific factors that influence the specific-sorption capacity of the soil (i.e. soil pH, organic matter content, clay mineralogy, texture) as well as the site drainage conditions. For example, Mann and Ritchie (1995) and Williams and David (1976) note the elevated risk of Cd leaching in low organic matter sandy soils due to their lack of adsorptive surfaces, with the latter reporting only 50% recovery of fertiliser-applied Cd in the cultivation layer of a coarse textured sandy soil. Similarly, recent research on a young stony soil (Carrick *et al.*, 2014) indicated that Cd leaching from large intact lysimeters (460 mm diameter, 700 mm depth) accounted for up to 42% of the Cd that was applied to the soil surface, although this was highly variable between individual lysimeters. These studies suggest that direct leaching of Cd can be much larger on coarse textured soils with limited Cd sorption capacity, or where bypass flow limits contact with sorption surfaces within the soil matrix. However, predicting risk of Cd leaching is both complex and conflicting; for example Gray *et al.*

(2003b) found no clear, consistent relationship between Cd leaching losses and any major soil property for six New Zealand soils (Table 2.8). Unfortunately the authors did not attempt to convert the Cd concentrations (mg kg^{-1}) of each soil to total soil Cd loads (g Cd ha^{-1}), which may provide a better relationship to Cd leaching risk between soils of contrasting bulk density.

2.4.1.4 Spatial variability in soil cadmium

Similar to other plant-essential nutrients, variability in soil Cd concentrations within pastoral systems might be expected to be driven by factors such as soil erosion, animal transfer, spatial variation in P fertiliser inputs, and variation in land use management with time (e.g. cropping / cultivation cycles within the pastoral system). However, relatively little research has been undertaken in New Zealand to quantify within-farm spatial variability of soil Cd concentrations. Three examples of soil Cd spatial variability work in hill country pastoral grazing systems are summarised in Table 2.9. One of these (Taylor and Percival, 2001) is specific to the isolated 'point-source' effect of Cd accumulation around a fertiliser storage bin.

Table 2.9. Summary of research on the spatial variability of soil Cd in New Zealand grazed pastoral systems.

Reference	Details	Findings
Loganathan *et al.* (1995)	A long-term hill country fertiliser trial site was used to assess variation in soil Cd with slope class (low [<13°], medium [13-25°], high [>25°]) and aspect	• Soil Cd was highest on low slopes and declined with increasing slope. The authors attributed this to lower inputs of P fertiliser per unit land area and reduced excretal returns as slope increased. • Overall, aspect did not have a statistically significant effect on soil Cd concentration. However the authors noted a trend for soil Cd to be higher on the east-facing slopes (in particular the low slope areas) where stock spent proportionally more time sheltering from the prevailing north-westerly wind.
Taylor and Percival (2001)	Cd concentration and speciation measured in soil samples collected along transects away from a fertiliser storage bin at a topdressing airstrip	• Soil Cd was enriched within 20 m of the fertiliser bin, with total Cd levels of 6.5, 5, 4.3 and 1.3 mg kg^{-1} at 1, 5, 10 and 20 m, respectively. Comparatively, at 45 and 100 m, soil total Cd had stabilised at 0.5 and 0.6 mg kg^{-1}, presumably indicative of the general soil Cd concentration within this property. • Cd^{2+} accounted for 55% to 90% of Cd in soil solution, increasing in predominance with increasing distance from the fertiliser bin. • Chloride and sulphate complexes accounted for the majority of the remaining Cd in soil solution. Cd-sulphate complexes diminished rapidly beyond 5-10 m distance from the fertiliser bin (consistent with soil solution SO_4^{2+} levels) indicating a proximity effect from deposition of superphosphate residues near the fertiliser bin.
Roberts and Longhurst (2002)	Assessment of spatial variability in soil Cd in sheep-grazed hill-country pastures	• Animal campsites had the highest soil Cd concentration (mean 0.49 mg kg^{-1}) followed by easy slopes and laneways (mean 0.32 mg kg^{-1}) and steeply sloping areas the lowest (mean 0.25 mg kg^{-1}). • It was proposed that Cd enrichment in animal campsites was partly due to Cd being deposited in animal faeces, in addition to reduced Cd loss in soil erosion / runoff due to the flatter topography in campsites. • In contrast, faecal deposition onto steep areas would be much lower with shorter grazing periods in these areas, and hence greater net Cd transport out of the steep slope areas would be expected to occur.

As more than 99% of Cd ingested by dairy cattle and sheep is excreted predominantly in faeces (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) animal transfer via non-uniform dung deposition is thought to be a significant factor contributing to spatial variability in soil Cd (Loganathan *et al.*, 1995; Roberts and Longhurst, 2002). This suggests that soil Cd accumulation is likely to occur in areas where concentrated deposition of animal faeces occurs, such as animal campsites, around stock congregation zones (e.g. shelter or water supply) and in effluent application zones within dairy farms.

The importance of concentrated dung deposition to Cd accumulation is exemplified by the findings for animal campsites of Roberts and Longhurst (2002). Using faecal deposition data for these campsites (12.6 t faecal DM ha^{-1} y^{-1} (Gillingham, 1980)) combined with the reported mean sheep faecal Cd concentration of 0.75 mg kg^{-1} (Roberts and Longhurst, 2002) faecal-Cd inputs into these animal campsites can be estimated at 9.4 g Cd ha^{-1} y^{-1}. In comparison, the maintenance P fertiliser at this site (250 kg ha^{-1} y^{-1} single superphosphate (Gillingham, 1980)) would apply 6.3 g Cd ha^{-1} y^{-1} (based on single superphosphate containing 9% P and 280 mg Cd kg^{-1} P). Assuming P fertiliser was also applied to the campsites, this would corroborate the significantly greater mean soil Cd concentrations reported for the campsite areas (Table 2.9).

No research appears to have been undertaken to quantify spatial variability of soil Cd under long-term dairy land use. This represents a significant knowledge gap, as this land use scenario is likely to have amongst the most enriched soil Cd concentrations (Taylor *et al.*, 2007; McDowell *et al.*, 2013; Cavanagh, 2014b) and therefore the greatest scrutiny under the TFMS.

2.4.2 Cadmium in New Zealand agricultural plant species

The introduction of the TFMS will assist management of long-term soil Cd accumulation in agricultural soils. However, to develop effective strategies for managing dietary Cd exposure in both livestock and humans, it is necessary to understand variability in plant Cd accumulation, and the relationships between plant tissue Cd accumulation and various soil properties that

influence Cd phytoavailability. This applies to animal forages as well as arable / horticultural food crops, since all agricultural land use is captured under the TFMS. In addition, exceedance of food standard maximum residue levels in any agricultural produce has potential to impact on export earnings and perceptions of New Zealand as a 'safe' food producing nation. With this in mind, this section reviews the current state of knowledge with respect to plant Cd accumulation in New Zealand agriculture.

2.4.2.1 Cadmium accumulation in different plant species and cultivars

Plant Cd accumulation research that has been reported for New Zealand (Table 2.10) is consistent with the general observation that monocotyledonous plants species tend to have lower Cd concentrations than dicotyledonous plant species (Bingham *et al.*, 1975). In addition, species within the Gramineae (e.g. ryegrass, wheat) and Leguminosae (e.g. white clover) families typically contain lower Cd concentrations than species within the Solanaceae (e.g. potato), Asteraceae (e.g. lettuce, chicory) and Brassicaceae (e.g. turnip, kale, swede) families (Smolders and Mertens, 2012).

Internationally, significant research into Cd accumulation in staple food crops (e.g. potatoes, wheat) has occurred due to their important contribution to human dietary Cd intake. However, there is little field data for these crops in New Zealand soils outside of two field surveys (Roberts *et al.*, 1995; Gray *et al.*, 2001) that were carried out almost two decades ago. At the time, these surveys showed that a small proportion (approximately 10%) of samples had Cd concentrations that exceeded food standard MLs. Most plant Cd accumulation research in New Zealand has focussed on ryegrass and white clover, due to the importance of these species as the cornerstone of our pastoral industry. These two species have consistently shown low vegetative tissue Cd concentrations, typically falling within the range of 0.1-0.3 mg kg^{-1} DM (Table 2.10). However, outside of ryegrass and white clover, there is very little information on

Cd accumulation in other forage or crop species that is specific to New Zealand soils and environmental conditions.

Table 2.10. Summary of New Zealand studies investigating accumulation of Cd in different plant species and cultivars within species.

Reference	Details	Findings
Crush and Evans (1990)	Glasshouse trial using a Pallic soil with 'little or no P fertiliser history'	• Mean Cd conc. for chicory of 3 mg kg^{-1} DM, which was not affected by change in soil pH • No soil Cd data was provided.
Roberts *et al.* (1994)	Field survey of Cd in grasses, legumes & weeds in 'native' (non-P fertilised) & 'pastoral' (P fertilised) sites	• For fertilised pastoral sites, mean tissue Cd conc. descended in the order weeds (0.28 mg kg^{-1} DM) > grasses (0.10 mg kg^{-1} DM) > legumes (0.06 mg kg^{-1} DM) • Mean Cd conc. in grasses & weeds was significantly correlated with soil Cd conc. • Mean Cd conc. of weed species was greater in pastoral than native sites (0.28 & 0.14 mg kg^{-1} DM, respectively).
Roberts *et al.* (1995)	Survey of Cd in vegetables (South Auckland) and wheat grain (mid-Canterbury)	• Edible tissue Cd conc. decreased in the order wheat grain > lettuce > potato = onion, with corresponding mean tissue Cd conc. of 0.07, 0.04, 0.02, 0.02 mg kg^{-1} FW, respectively. • Around 10% of lettuce & wheat samples exceeded the current ML* of 0.1 mg kg^{-1} FW. Although less frequent, some potato & onion samples also exceeded this ML.
Loganathan *et al.* (1995)	Field trial site that had received high (765 kg P ha^{-1}) or low (113 kg P ha^{-1}) P fertiliser input over 20 years	• Pasture Cd conc. reflected historic Cd inputs in P fertiliser. Mean pasture Cd conc. on the high-P farmlet (0.321 mg kg^{-1} DM) was 5 times higher than the low-P farmlet (0.063 mg kg^{-1} DM). • Low slope areas were dominated by ryegrass / white clover, with mean pasture Cd conc. ranging between approximately 0.05-0.22 mg kg^{-1} DM
Lee *et al.* (1996)	Field trial	• Fertilised ryegrass/white clover dominant pasture with plant tissue Cd conc. ranging between 0.12-0.3 mg kg^{-1} DM.
Loganathan *et al.* (1997)	Long term P fertiliser field trial	• Mean Cd conc. in grass & clover ranged between approximately 0.025-0.225 mg kg^{-1} DM & 0.01-0.085 mg kg^{-1} DM, respectively.
Gray *et al.* (1999a)	Pot trials assessing Cd accumulation in various plant species, for 10 different soil types.	• Plant Cd conc. decreased in the order: lettuce > carrot top > carrot root > lucerne > cabbage > wheat > maize > ryegrass > clover > barley • Cd conc. in lucerne was ~3 times higher than ryegrass & white clover • Plant Cd conc. were generally highest for two Allophanic soils that had much greater soil Cd conc. (0.74 & 1.34 mg kg^{-1}) than the other soils studied (0.03-0.45 mg kg^{-1})
Gray *et al.* (1999c)	Pot trials assessing effect of soil pH on Cd accumulation in 5 plant species across 3 soils	• Cd conc. decreased in the order lettuce >> carrot top > carrot root > wheat straw = ryegrass = clover > wheat grain • Plant Cd conc. descended in the order Granular soil > Allophanic soil > Recent soil, despite soil total Cd conc. being much higher in the Allophanic soil. The high soil Cd conc. & low pH of the Allophanic soil may have been offset by its higher organic carbon & clay mineralogy. • Cd conc. decreased with increasing soil pH • Cd accumulation in lettuce was ~4 times higher than other species • Cd in wheat grain was ~50-80% lower than in the straw
Gray *et al.* (2001)	Field survey of grain Cd concentrations in wheat cultivars grown throughout New Zealand	• Average Cd conc. of wheat grain was ~0.054 mg kg^{-1} FW • Approx. 10% of samples exceeded the current ML of 0.1 mg kg^{-1} FW. Around half of these exceedances were from 1 site that had more greatly enriched soil Cd conc. (0.26-0.33 mg kg^{-1}). • A four-fold difference in grain Cd accumulation between cultivars. 'Monad' had the highest grain Cd conc., around 50-60% higher than the next highest cultivar.
Roberts and Longhurst (2002)	Field survey	• Fertilised easy slopes and stock camps dominated by ryegrass / white clover, with pasture Cd conc. ranging between ~0.1-0.3 mg kg^{-1} DM.
Gray and McLaren (2005)	Pot trial assessing Cd accumulation in various ryegrass cultivars	• Cd conc. varied approximately 2-fold between various ryegrass cultivars. • Short rotation (2-3 year) & annual ryegrass cultivars contained the lowest Cd conc., which the authors partly explained by their higher growth rates (greater dilution).
Parker *et al.* (2008)	Field trial	• Cd conc. was around 4-5 times higher in a plantain / chicory / red clover / white clover forage stand (0.36-0.75 mg kg^{-1} DM) than in a corresponding ryegrass / white clover pasture (0.11-0.22 mg kg^{-1} DM). • No species-specific data presented and no soil Cd data presented
Reiser *et al.* (2014)	Field survey of 69 dairy / intensive cattle pastures	• 90% of ryegrass dominant pastures had Cd conc. less than 0.2 mg kg^{-1} DM, with a mean of 0.13 mg kg^{-1} DM. • Plant tissue Cd conc. was only weakly correlated (R = 0.31) to soil total Cd conc.

*ML = maximum level of a contaminant that is permitted in a specified food product (FSANZ, 2013).

From a national survey of pastoral and native sites, Roberts *et al.* (1994) reported that tissue Cd concentrations descended in the order weeds > grasses > legumes. Unfortunately, these authors did not report Cd results for individual species, particularly since plantain (now a common specialist finishing and summer feed crop) was noted as one of the key 'weed' species in the survey. Reinforcing this observation, Parker *et al.* (2008) reported that the Cd concentration of a mixed plantain / chicory / red clover / white clover forage stand (0.36-0.75 mg kg^{-1} DM) was approximately four to five times higher than in an adjacent ryegrass / white clover pasture (0.11-0.22 mg kg^{-1} DM), although again, no species-specific plant Cd data (or soil Cd data) was presented. Notably, Crush and Evans (1990) also reported a very high tissue Cd concentration for chicory (3.0 mg kg^{-1} DM) despite being grown in a soil with 'little or no P fertiliser history' (no soil Cd data was presented). This suggests chicory has ability to sequester and transfer Cd to vegetative tissues, even at 'natural-background' soil Cd concentrations.

The limited international data that exists on Cd accumulation in chicory and plantain reaffirms the status of these species as efficient shoot Cd translocators. For example, Martin *et al.* (1996) and Simon *et al.* (1996) found that chicory can accumulate relatively high leaf Cd concentrations (1.6-2.4 mg kg^{-1} DM) even at relatively low 'background' soil Cd concentrations. Where Cd phytoavailability was artificially increased (for example, contaminated soils or those purposefully amended with Cd-salts) chicory was capable of accumulating much greater leaf Cd concentrations (Martin *et al.*, 1996; Simon *et al.*, 1996; Sękara *et al.*, 2005; Abe *et al.*, 2008; Bešter *et al.*, 2013). Caution needs to be exercised in extrapolating these results to New Zealand conditions, due to artificially high soil Cd phytoavailability, as well as soil and cultivar differences. However, these studies do reinforce that chicory and plantain are Cd-accumulating species that are sensitive to increased soil Cd phytoavailability.

Various brassicas crops (e.g. turnip, kale, swede) are also integral forage components within many New Zealand grazing systems. Currently, there is a dearth of local information on Cd accumulation in these plant species, although limited international data suggests turnip is an

efficient shoot Cd translocator, being capable of expressing high Cd concentrations in leaf tissue (> 1.0 mg kg^{-1} DM) although Cd concentrations in the bulbs (0.1-0.2 mg kg^{-1} DM) are generally much lower (Singh and Nayyar, 1990; De Pieri *et al.*, 1997).

2.4.2.2 Variability in plant tissue Cd concentration

2.4.2.2.1 Spatial variation in pastoral Cd concentration

Similar to soils, knowledge of spatial variability in plant tissue Cd concentrations within farm systems is also limited to a few studies in hill country sheep and beef systems. In general, these papers indicate that within a farm, soil total Cd concentration is poorly correlated with pasture Cd concentration, due to spatial variation in pasture species composition as well as soil properties that influence Cd sorption and phytoavailability. For example, Roberts and Longhurst (2002) found soil total Cd to be highest in stock camps and lowest in steep slope areas. However, the opposite effect occurred for plant tissue Cd concentrations, with the lowest pasture Cd levels reported in stock camp areas (mean 0.18 mg kg^{-1}) and highest in steeply sloping areas (mean 0.41 mg kg^{-1}). Similarly, Loganathan *et al.* (1995) also reported that pasture Cd content increased with increasing slope class. These authors attributed this spatial variability to several possible mechanisms:

i. Stock camps had low weed content and high ryegrass content in the sward whereas steep slopes had high weed content and fewer grasses, citing Roberts *et al.* (1994) who reported weed species to have higher Cd content than grasses and clover (Table 2.10).
ii. Pasture production was much higher in the stock campsites, effectively diluting tissue Cd concentration in these areas.
iii. Soil extractable Cd as a percentage of total Cd was lower in campsites than in steeply sloping areas, possibly related to higher soil carbon and pH in the campsites.
iv. In steep areas the dominant grass species are low-fertility tolerant species (e.g. browntop and sweet vernal) which Loganathan *et al.* (1995) proposed may accumulate

greater tissue Cd concentrations due to lower growth rates than high-fertility dependent species such as ryegrass.

2.4.2.2.2 Seasonal variation in pastoral Cd concentrations

Pasture Cd concentrations have shown large seasonal variation. Loganathan *et al.* (1997) found pasture Cd levels to be highest in autumn and lowest in late-spring/early summer, with ryegrass exhibiting a two- to three-fold variation in Cd concentration throughout the year. Similarly, data of Roberts and Longhurst (2002) showed that highest pasture Cd levels occurred in autumn. These findings are consistent with the theme of international literature, which indicate plant Cd concentrations are generally inversely related to plant growth rate / yield (Section 2.3.3). However, in addition to growth rate and consequent dilution effects, Loganathan *et al.* (1997) commented that seasonal variation could be related to other factors such as change in pasture composition or change in soil moisture affecting soil Cd sorption dynamics, although there is little substantive evidence to support the latter mechanism. Plant morphological change could also be responsible for seasonal variation in plant Cd concentrations, as numerous authors (He and Singh, 1994; Oborn *et al.*, 1995; De Pieri *et al.*, 1997; Gray *et al.*, 1999c) have reported that Cd concentrations are greater in the vegetative tissues (i.e. the stem and leaves) than reproductive tissues (i.e. seed / fruit).

2.4.2.2.3 Direct effects of recent P fertiliser application on plant Cd uptake

The influence of historic P fertiliser application intensity on soil Cd accumulation is well documented (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan *et al.*, 1997; Gray *et al.*, 1999b). However, the direct influence on plant Cd uptake/accumulation resulting from freshly applied, soluble Cd inputs in P fertiliser is less obvious. Williams and David (1976) noted that only 1-5% of soluble Cd applied to the soil is recovered by the plant, which is supported by other international studies that have found little difference in plant Cd accumulation between P fertilisers with different Cd concentrations (Sparrow *et al.*, 1993b; McLaughlin *et al.*, 1995).

Conversely, other studies have found significant increases in plant tissue Cd concentration with increasing rate of soluble Cd applied (Williams and David, 1973; Mortvedt *et al.*, 1981; Sparrow *et al.*, 1992; Sparrow *et al.*, 1993a; Maier *et al.*, 2002).

This discrepancy may be partly explained by differences in background soil Cd (and P) availability as well as differences in fertiliser Cd-solubility. Furthermore, P fertilisers that acidify the soil at the point of dissolution are likely to temporarily reduce Cd adsorption and induce greater plant Cd uptake, relative to P fertilisers such as DAP that temporarily create an alkaline soil environment upon dissolution (Reuss *et al.*, 1978; Levi-Minzi and Petruzzelli, 1984). This effect may be further compounded where the presence of other cations (e.g. soluble calcium associated with monocalcium phosphate in superphosphate) may competitively interact with Cd for sorption sites.

With respect to New Zealand pastoral systems, the potential for short term increases in pasture Cd concentration following P fertiliser application does not appear to have been assessed. Coincidentally, the autumn spike in pasture Cd concentration reported by Loganathan *et al.* (1997) and Roberts and Longhurst (2002) also coincides with the timing of P fertiliser application at these field trial sites, although neither study draws comment on any potential linkage. Extrapolating from the data presented by Roberts and Longhurst (2002), using the stated P fertiliser Cd content of ~170 mg Cd kg^{-1} P, around 3400 mg Cd ha^{-1} would be introduced at an application rate of 20 kg P ha^{-1}. In comparison, the approximate doubling of herbage Cd (from ~0.17 mg kg^{-1} to ~0.34 mg kg^{-1}) that occurred between March and April for pasture receiving 20 kg P ha^{-1} would only require an additional 153-255 mg Cd ha^{-1} to be taken up (based on 30 days growth assuming a pasture growth rate of 30-50 kg DM ha^{-1} d^{-1}). It therefore seems plausible that a short term spike in herbage Cd could occur subsequent to P fertiliser application; however without radioisotope tracer data this is purely speculative, and it appears little research has been carried out on this aspect.

2.4.2.3 Assessing soil cadmium phytoavailability

While soil total Cd concentration is generally considered to be an important factor influencing plant Cd uptake (Roberts *et al.*, 1994; McBride *et al.*, 1997; Gray *et al.*, 1999a, d; McBride, 2002) many soil-specific physical and chemical factors influence Cd sorption-desorption processes and Cd phytoavailability, as discussed in Section 2.2. In an attempt to better explain variation in plant tissue Cd concentration, various soil extractants (and extraction methodologies) have therefore been assessed for their ability to predict the phytoavailable soil Cd fraction. Examples of such studies carried out using New Zealand soils are summarised in Table 2.11.

Table 2.11. Summary of New Zealand research investigating relationships between extractable soil Cd and plant Cd tissue concentrations.

Reference	Details	Findings
Roberts *et al.* (1995)	Survey of vegetable & cereal crops	• Poor relationship between 0.05 M $CaCl_2$-extractable soil Cd and Cd content in market garden crops (R^2 = 0.17) and cereal grain (R^2 = 0.04)
Andrewes *et al.* (1996)	Cd accumulation in lettuce in pot trials using 9 different soils, 5 extractants and 2 measurement techniques	• Total Cd was poorly correlated with tissue Cd concentration • $CaCl_2$ extraction provided the strongest correlation with tissue Cd concentration, since this extractant did not affect pH, provided cations to exchange with non-specifically sorbed Cd, was non-destructive to most minerals & did not strongly complex Cd. • For 0.01 M $CaCl_2$, correlation was strongest when the total Cd in extracted solution was measured (graphite furnace atomic absorption spectrophotometry technique) • For 0.05 M $CaCl_2$ extraction, correlation was strongest when only free Cd^{2+} ions and labile Cd in extracted solution was assessed.
Gray *et al.* (1999a)	8 soil extractants assessed across 10 soil types for their correlation with Cd in various vegetable, cereal & pasture species grown in pots	• Significant relationships between extracted Cd and plant tissue Cd levels existed for all extractants. However, the significance of the correlation depended on plant species and varied with extractant. • Across all plant species 0.05 M $Ca(NO_3)_2$ was found to be the best predictor of plant Cd concentration, although the overall correlation was weak (R^2 = 0.32). • In many cases, the significance of the correlation between soil total Cd and plant Cd was as strong as the best extractable-Cd measures.
Gray *et al.* (1999c)	8 soil extractants assessed across 3 soil types at 3 pH levels for their correlation with Cd in various vegetable, cereal & pasture species grown in pots	• Strength of correlation between extractable soil Cd and plant tissue Cd differed with plant species and extractant • Weaker extractants (0.01 M $CaCl_2$ and 1 M NH_4NO_3) were unreliable, probably because they could not extract sufficient Cd from the soil, while an acid extractant (0.05 M AAAc-EDTA) was unreliable since it was insensitive to soil pH change • The most reliable extractants were those sensitive to soil pH or which extracted moderate amounts of soil Cd (0.05 M $Ca[NO_3]_2$, 1 M NH_4OAc, 1 M NH_4Cl, 0.05 M $CaCl_2$, 0.04 M EDTA) • Soluble Cd as determined by the equation of Gray et al. (1999c) that takes into account soil total Cd, pH, and organic matter content, was often found to be most successful in predicting plant Cd concentration
Reiser *et al.* (2014)	Survey of 69 intensive cattle & dairy pastures	• Correlation with pasture Cd concentration was stronger for 0.05 M $Ca(NO_3)_2$-extractable soil Cd (R = 0.41) than soil total Cd (R = 0.31) • However best-fit multiple regression analysis was only able to explain 38% of the variation in pasture Cd concentrations overall.

For horticultural / arable food crops where occasional exceedance of food standard Cd MLs has been reported (Roberts *et al.*, 1995; Gray *et al.*, 2001) there is particular need for robust

assessment of phytoavailable soil Cd, from which to base crop selection and land management decisions. However, the general conclusion drawn from the literature is that predicting soil Cd phytoavailability remains challenging across soils with different properties, as well as across different plant species, since the strength of the relationship with plant tissue Cd concentration varies by plant species (Gray et al., 1999a).

Of eight different soil Cd extractants appraised by Gray *et al.* (1999a), 0.05 M $Ca(NO_3)_2$ was the most successful extractant when assessed across a range of plant species. However, there was little difference in performance between 0.05 M $Ca(NO_3)_2$ and 0.05 M $CaCl_2$, with the latter extractant being more robust for the pastoral species assessed (ryegrass, clover and lucerne). While soil total Cd in isolation is unlikely to have a strong correlation with plant Cd accumulation across different soil types and plant species, its combination with other soil factors (e.g. pH, organic matter) may be sufficient for predicting soil Cd solubility / phytoavailability risk across contrasting soils (McBride *et al.*, 1997; Gray *et al.*, 1999a, c).

2.4.3 Cadmium accumulation in grazing livestock

Although more than 99% of Cd ingested by grazing livestock has been shown to be excreted (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) Cd that is absorbed via the gastrointestinal tract has been shown to accumulate primarily in the liver and kidneys (Solly *et al.*, 1981; Lee *et al.*, 1994; Lee *et al.*, 1996). The reason for this is that relative to other tissues, the kidney and liver produce large amounts of metallothionein, a metal-binding protein involved in transport and storage of Cd (Petering and Fowler, 1986). The high capacity for metallothionein synthesis allows these organs to act as filters, sorbing Cd and other metals and removing them from further circulation, thus providing a means to regulate against potentially toxic metal concentrations (Petering and Fowler, 1986). Research has shown that metallothionein synthesis is highly responsive to dietary Cd load. For example, increased dietary Cd exposure increased metallothionein production and consequent Cd accumulation in

the liver and kidney of sheep, whilst Cd accumulation in muscle tissues concurrently decreased (Lee *et al.*, 1994; Lee *et al.*, 1996).

Efficient Cd deposition in the liver and kidney minimises risk of inter-generational bioaccumulation. For example, Cd accumulation in foetal and new born lambs has been shown to be very low and unrelated to dietary Cd intake of the mother, explained by a lack of placental Cd transfer (Rounce *et al.*, 1995) and low concentration of Cd in ewes milk (Rounce *et al.*, 1997). Similarly, Cd is only expressed in very low concentrations in the milk of dairy cattle and milk Cd concentration does not appreciably increase with increased dietary Cd intake (Sharma *et al.*, 1982; Morrison, 1988). On-going routine monitoring for contaminants in milk products in New Zealand has indicated that Cd is generally below the limit of detection of 0.002 mg L^{-1} (MPI, 2012). This suggests that due to the efficiency of the liver and kidney at binding Cd, there is little risk of elevated human dietary Cd exposure via dairy produce.

The sorption and retention of Cd in livestock liver / kidney tissue does mean that consumption of these animal offal products could increase human dietary Cd exposure. An early abattoir survey (1988-1991) revealed that 22-28% of sheep kidneys and 14-20% of cattle kidneys exceeded 1 mg Cd kg^{-1} FW (the New Zealand food standard ML at the time). As livestock liver / kidney Cd concentration was determined to increase with increasing age (Lee *et al.*, 1994; Roberts *et al.*, 1994; Lee *et al.*, 1996) the New Zealand meat industry began screening kidneys intended for human consumption, discarding these from animals aged 30 months or older, so as to minimise risk of food standard ML exceedances, as well as manage potential risks to export trade (Roberts *et al.*, 1994; MAF, 2008). However, as the rate of Cd accumulation is greater in young animals and directly influenced by the daily dietary Cd intake (Lee *et al.*, 1994; Lee *et al.*, 1996) (Figure 2.3), there is risk that kidneys from livestock less than 30 months of age could still exceed food standard ML's. Supporting this, Lee *et al.* (1994) reported that more than 22% of kidneys from young sheep (<30 months) exceeded 1 mg Cd kg^{-1} FW (the current European Union (EU) food standard ML).

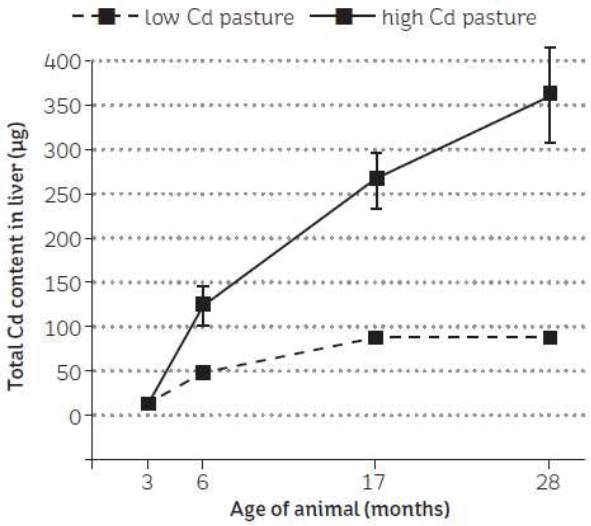

Figure 2.3. Cd content in the liver of lambs aged 3, 6, 17, 28 months, after feeding low-Cd (mean 0.18 mg kg^{-1} DM) or high-Cd (mean 0.52 mg kg^{-1} DM) pasture from 3 months of age (Lee *et al.*, 1996).

2.4.3.1 Contribution of forage versus soil ingestion to livestock Cd intake

Although soil ingestion also contributes to the total dietary Cd intake of grazing livestock, this contribution is small relative to that via the plant tissue animals consume. For example, Roberts and Longhurst (2002) determined soil ingestion to account for only 3% and 6% of total dietary Cd load for lax and hard grazed ewes, respectively. Lee *et al.* (1996) determined that soil ingestion during winter and summer accounted for about 14% and <2% of total dietary Cd load, respectively. While a minor overall contribution to total dietary Cd intake, these studies indicate that grazing management can influence animal Cd accumulation. In particular, this may be the case where livestock are grazing bulb-forming forage crops such as turnips and swedes, where a large proportion of the total dry matter ration is in close contact with the soil.

2.4.4 Modelling Cd accumulation

Modelling soil-plant-animal Cd transfer and accumulation is an important step in developing effective management strategies. The advantage of scenario modelling is that it can allow landowners to predict undesirable effects in advance, allowing them to put preventative

measures in place. This is preferable to reacting based on observation, since it can be far more costly and difficult to mitigate an effect than to prevent it from occurring in the first place.

2.4.4.1 Soil Cd accumulation - CADBAL

The TFMS caters for a modelling approach to guide site-specific soil Cd accumulation risk assessment once soil Cd concentrations exceed 'tier 0' (0.6 mg kg^{-1}). For this purpose, CADBAL is a soil Cd mass-balance model that was developed in the 1990's by the Fertiliser Manufacturers Research Association (Roberts and Longhurst, 2005). To quantify the net Cd accumulation rate in agricultural soils, CADBAL takes into account soil input factors (P fertiliser type and rate, atmospheric deposition, application of biosolids), soil retention factors (e.g. clay content/types, organic matter content), and soil loss factors (e.g. plant uptake and removal in either produce or transfer by grazing animals, particulate erosion, and dissolved Cd losses removed from the soil via overland flow or leaching).

Unfortunately, there is a paucity of data for several key variables to which CADBAL is highly sensitive (e.g. soil erosion and Cd leaching data relevant for many soil orders (Cavanagh, 2014a)). Research has recently been initiated to help close some of these gaps (Carrick *et al.*, 2014; Gray and McDowell, 2016). Furthermore, only limited validation of CADBAL has occurred. Roberts and Longhurst (2005) compared actual soil Cd accumulation data from the Winchmore long-term fertiliser trial site with predictions generated by CADBAL. It was found that CADBAL over-predicted soil Cd accumulation for the first 24 years of data, and thereafter under-predicted soil Cd accumulation. The authors noted the underlying sensitivity of CADBAL predictions to the Cd content of fertiliser applied, which made validation difficult since fertiliser samples had not been archived for Cd analysis. More recently, McDowell (2012) repeated the validation process using refined base data for Winchmore, which had become available subsequent to the original validation of Roberts and Longhurst (2005). This consisted of changes to inputs including pasture production, Cd leaching losses, atmospheric deposition

of Cd, sediment erosion losses, and fertiliser Cd concentration. With these improvements, McDowell (2012) commented that CADBAL predictions gave a 'reasonable fit' to the measured data, provided that robust data was used in the modelling process. This reinforces the critical importance of input data integrity, an issue common to all modelling approaches.

2.4.4.2 Animal Cd accumulation

The first attempts to model animal Cd accumulation (Bramley, 1990) were thwarted by the lack of robust data relevant to New Zealand's grazed pastoral systems. Subsequent research to generate this dataset allowed Lee *et al.* (1996) and Loganathan *et al.* (1999) to develop models that could successfully describe Cd accumulation in the liver and kidney of sheep.

Based on a 25-month animal grazing trial with freshly weaned lambs exposed to low (0.18 ± 0.08 mg Cd kg^{-1} DM) or high (0.52 ± 0.17 mg Cd kg^{-1} DM) Cd pastures (spiked using $CdSO_4$), Lee *et al.* (1996) developed models that were successful in predicting sheep kidney (Equation 1) and liver (Equation 2) Cd accumulation:

$$Kidney_{Cd} = -205 + 0.981Cd_{Intake} + 0.726Time \quad (P < 0.001, R = 0.82) \quad (1)$$

$$Liver_{Cd} = 24.7 + 0.353Cd_{Intake} \quad (P < 0.001, R = 0.81) \quad (2)$$

Where $Kidney_{Cd}$ and $Liver_{Cd}$ are the Cd concentrations (ng g^{-1} FW) predicted for these tissues, Cd_{Intake} is the amount of Cd ingested on a daily basis (μg day^{-1}), and *Time* is the number of days (post weaning) that the animal is exposed to this dietary Cd intake.

Although both the liver and kidney Cd accumulation regression models were highly sensitive to the variable Cd_{Intake} (daily dietary Cd intake), the variable *Time* (number of days that stock were exposed to the daily dietary Cd intake) only reached significance for the kidney Cd accumulation dataset. The sensitivity of these lamb kidney and liver Cd accumulation models to dietary Cd intake is exemplified in Figure 2.4, representing 7 month old lambs nearing slaughter (i.e. 120 days grazing post-weaning). In this scenario, the models predict that 7

month old lambs would exceed the EU ML for kidney and liver (1.0 and 0.5 mg Cd kg^{-1} FW, respectively (EC, 2014)) when consuming feed containing between 1 - 1.5 mg Cd kg^{-1} FW, respectively.

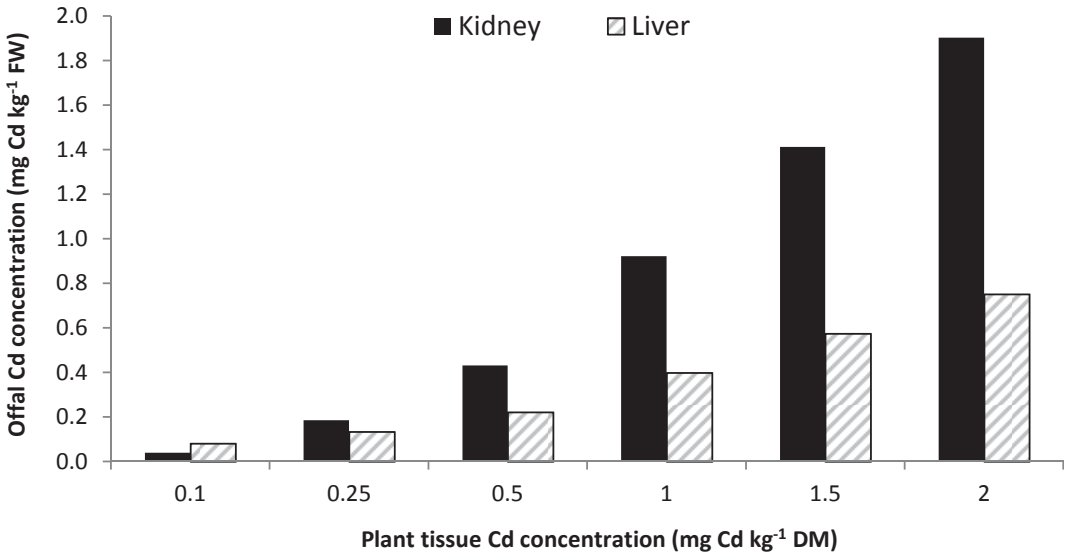

Figure 2.4. Influence of plant tissue Cd concentration on Cd accumulation in lamb kidney and liver, as predicted using the models of Lee *et al.* (1996). Assumed model parameters: feed intake = 1 kg DM d^{-1}, soil intake = 0.1 kg DW d^{-1}, soil Cd concentration = 0.6 mg kg^{-1} DW, Time = 120 days (post weaning).

Loganathan *et al.* (1999) reported a strong correlation between modelled and measured kidney Cd accumulation using data from a long-term grazed fertiliser trial. Their model suggested that for Cd-enriched soils (0.55 mg kg^{-1} DW) and the corresponding pasture (0.15-0.3 mg kg^{-1} DM) Cd in the kidneys of animals aged 18-24 months could potentially exceed 1 mg kg^{-1} FW, aligning with findings from an earlier abattoir survey (Lee *et al.*, 1994; Roberts *et al.*, 1994). More recently, Reiser *et al.* (2014) combined data from a field survey of Cd in New Zealand soils and ryegrass-dominant pastures with a European heavy metal accumulation model (Rodrigues *et al.*, 2012) (Equation 3) to determine the likely frequency that offal Cd concentrations would breach food standard MLs:

$$ADI_{Cd} = ([Cd]_{limit\ in\ animal\ organ} \times (I_{feed} + I_{soil})) \div (BAF_{feed\ -\ animal\ organ}) \quad (3)$$

Where ADI_{Cd} is the Acceptable Dietary Intake of Cd (mg d^{-1}) for grazing livestock to maintain liver / kidney Cd concentrations below the relevant food standard ML, $[Cd]_{limit\ in\ animal\ organ}$ is the relevant food standard Cd ML (NZ: 2.5 mg kg^{-1} kidney FW & 1.25 mg kg^{-1} liver FW. EU: 1.0 mg kg^{-1} kidney FW & 0.5 mg kg^{-1} liver FW), I_{feed} and I_{soil} is the daily animal intake of feed (kg DM d^{-1}) and soil (kg DW d^{-1}), and *BAF* is a bioaccumulation factor, defined as the Cd concentration in the animal organ (mg Cd kg^{-1} FW) divided by the Cd concentration in the feed (mg Cd kg^{-1} DW). Reiser *et al.* (2014) used *BAF* values taken from de Vries *et al.* (2007), which represented the upper end of ranges reported by other authors (Cow: kidney = 2.99, liver = 0.554; Sheep: kidney = 2.08, liver = 1.85).

Using this approach, Reiser *et al.* (2014) reported that actual dietary Cd intakes exceeded the ADI_{Cd} (and as such, food standards MLs would be breached) in a small number of cases (up to 7.2% of sites sampled, for the more restrictive EU liver Cd ML of 0.5 mg kg^{-1} FW). Again, this finding is consistent with previous abattoir survey data (Lee *et al.*, 1994; Roberts *et al.*, 1994) as well as the modelling results of Loganathan *et al.* (1999).

The acceptable dietary Cd intake model of Rodrigues *et al.* (2012) and the sheep liver Cd accumulation model of Lee *et al.* (1996) (Equation 3 and 2, respectively) do not consider the age of the animal or the time period over which the dietary Cd exposure occurs. As such, while these models may predict whether food safety standards are likely to be breached based on animal dietary Cd intake, they are of little value in determining how quickly this breach will occur. Although the kidney Cd accumulation model of Lee et al. (1996) (Equation 1) factors in the time period over which livestock are exposed to the designated dietary Cd intake, the model becomes relatively insensitive to the 'time' variable at plant tissue Cd concentrations of 0.5 mg kg^{-1} DM or greater. This may be the consequence of plant tissue Cd concentrations of this magnitude being outside the range of the models calibration dataset. This is a common weakness of existing New Zealand livestock Cd accumulation models, which have been based

on ryegrass/white clover pastures containing relatively low tissue Cd concentrations (typically <0.3 mg kg^{-1} DM; Table 2.10).

Based on the positive relationship between dietary Cd intake and livestock Cd accumulation established by Lee *et al.* (1996), if different forage species now used in New Zealand livestock grazing systems accumulate greater tissue Cd concentrations than ryegrass-white clover pastures (which the original models were based upon), then ruminant kidney / liver Cd accumulation and food standard ML exceedance may be greater than that previously predicted. Alternatively, there is also the possibility that the original livestock Cd accumulation models that were based on ryegrass-dominant diets are no longer robust when applied to different forage crops, since these may impart differing animal Cd absorption/retention coefficients (Parker *et al.*, 2008). Given the lack of Cd accumulation data for many of the plant species now commonly used as animal forages, establishing this dataset has been recommended as a first step to improve the accuracy of animal Cd accumulation risk assessment models (Reiser *et al.*, 2014).

2.5 Summary

Cadmium accumulation in New Zealand soils has been linked primarily with P fertiliser usage (Bramley, 1990; Roberts *et al.*, 1994; Loganathan *et al.*, 2003). To assist management of on-going Cd accumulation, a Tiered Fertiliser Management System (TFMS) has been implemented in New Zealand as part of a new National Cadmium Management Strategy (MAF, 2011). Within the TFMS, as soil total Cd concentration increases, increasing restrictions on P fertiliser management apply, so as to manage further soil Cd accumulation (MAF, 2011). Previous research has indicated that traditionally-intensive farmland with a rich history of P fertiliser inputs is likely to have the most elevated soil Cd concentrations (Roberts *et al.*, 1994; Taylor *et al.*, 2007; McDowell *et al.*, 2013; Cavanagh, 2014b). On this basis, long-term dairy farms on Allophanic, Pumice and Organic soil orders are likely to have amongst the most enriched soil

Cd concentrations, and are therefore likely to be most impacted by the TFMS. However, currently there is no data available to understand how soil Cd concentrations vary within these farms systems, and therefore, how soil sampling should be best managed to provide a robust soil Cd appraisal under the TFMS.

Furthermore, while managing soil Cd accumulation is a desirable outcome, it is the uptake and accumulation in plants that is the fundamental issue with respect to livestock and human dietary Cd exposure. A limitation of the TFMS is that it is based solely on soil total Cd with no recognition of other factors such as soil pH, organic matter and clay mineralogy, which are known to influence Cd sorption behaviour, solubility and phytoavailability (McBride, 1989; Gray *et al.*, 1999d; Loganathan *et al.*, 2012). While soil pH is thought to be the single most important factor influencing Cd phytoavailability (Loganathan *et al.*, 2012; Young, 2012) little field research has been carried out to quantify the effect (magnitude and speed) of soil pH manipulation on plant tissue Cd accumulation. Furthermore, while soil redox potential is known to influence metal solubility (Ponnamperuma, 1972), most research on Cd phytoavailability has occurred under extended periods of soil saturation typical of rice cultivation (de Livera *et al.*, 2011; Zhang *et al.*, 2012; Zheng *et al.*, 2013). Currently there no research quantifying the influence of fluctuating soil moisture (characterised by only short periods of saturation) on soil Cd phytoavailability, which is more relevant to New Zealand agricultural soil conditions.

As a consequence, the TFMS in its current guise is unlikely to adequately describe risk of plant Cd uptake and accumulation across soils of different total Cd concentrations and Cd-sorption characteristics. Furthermore, it is well documented that different plant species and cultivars within species have differing ability to accumulate Cd in above ground vegetative tissues (Bingham *et al.*, 1975; Gray *et al.*, 1999a; Gray *et al.*, 2001; Gray and McLaren, 2005; Smolders and Mertens, 2012). However, the literature has revealed that there is a shortage of Cd accumulation data for different forage species and cultivars (outside ryegrass, clover and

wheat) used in modern pastoral grazing systems, which is a limitation to robust animal Cd accumulation modelling (Reiser *et al.*, 2014).

It is important that we improve our understanding of these factors so that it is possible to develop robust, objective and farm-specific Cd management strategies to minimise risk of Cd transfer to the human diet.

2.5.1 Conclusions and research questions

This literature review has revealed three key knowledge gaps that with further research would help to improve and inform Cd management in New Zealand agricultural systems. The first of these is the need to better quantify spatial variability of soil Cd in long-term dairy farms, since these are likely to have amongst the most enriched soil Cd levels. Specifically, the following research questions have been identified:

i. How does soil Cd vary spatially (e.g. inter-paddock, intra-paddock) in well fertilised, long-term dairy pasture soils?
ii. Can soil Cd spatial variability be accounted for by appropriate delineation of land management units based on detailed soil and topographic maps and management history?
iii. How does Cd distribution vary with soil depth in well fertilised, long-term dairy pasture soils that have contrasting Cd status and Cd specific sorption capacity?
iv. What effect does dairy shed effluent application have in Cd cycling and soil Cd accumulation within grazed dairy systems?

Secondly, there is shortage of data on Cd uptake and accumulation in animal forage species other than ryegrass and white clover. In particular, plantain and chicory as well as brassicas (e.g. turnip and kale) which are now integral components in many farm systems. Improving this data set may help to improve quantification of livestock Cd accumulation risks when grazing these crops, and to inform practical farm management strategies to manage livestock dietary Cd exposure. The following research questions have been identified:

v. At equivalent soil Cd concentration, do any common animal forage species and/or cultivars accumulate greater tissue Cd concentrations, relative to ryegrass and white clover?

vi. How is plant tissue Cd concentration influenced by soil total Cd concentration and soil characteristics that influence soil Cd phytoavailability? (e.g. pH, organic matter, CEC). Can plant tissue Cd concentration be predicted from these soil variables?

vii. Is there a risk of accelerated Cd accumulation in animal offal products (i.e. liver and/or kidney) to stock grazing different forage species?

The third knowledge gap identified by the literature review relates to how site, environmental and management/mitigation factors influence soil Cd phytoavailability and plant Cd accumulation. Specifically, the following research questions have been identified:

viii. How does fluctuating soil moisture (characterised by only short periods of soil saturation) influence soil Cd phytoavailability and plant Cd accumulation?

ix. Can Cd uptake and accumulation in animal forage species be manipulated (either increased or decreased) by modifying soil pH? How quickly can this effect occur, and does the magnitude of pH influence vary for different forage plant species?

The research described in this thesis has been designed and conducted to explore and (where possible) answer these research questions.

CHAPTER 3 : Variability of soil cadmium in two long-term dairy farms

This chapter was summarised and submitted to Agriculture, Ecosystems and Environment in August 2017. It has been provisionally accepted, pending a reduction in content and other minor edits. Citation:

Stafford, A.D., Palmer, A.S., Jeyakumar, P., Hedley, M.J., Anderson, C.W.N., 2017. Soil cadmium and New Zealand dairy farms: impact of whole-farm contaminant variability on environmental management. Agriculture, Ecosystems and Environment (Submitted)

3.1 Abstract

Two long-term dairy farms in the North and South Island of New Zealand were studied to understand factors influencing variability in soil Cd concentrations between and within farm. Intensive soil sampling within each farm showed that soil Cd concentrations (0-150 mm depth) were much greater and more variable in the Waikato property (mean: 1.04 mg kg^{-1}, range: 0.48-1.64 mg kg^{-1}) than the Canterbury property (mean: 0.34 mg kg^{-1}, range: 0.15-0.64 mg kg^{-1}). Variation in soil Cd concentrations was primarily driven by variation in historic P fertiliser management practices and soil type. Slope class (only a factor in the Waikato farm) only exerted an influence on soil total Cd concentrations when slope exceeded 15°. No clear trends in soil Cd concentration could be determined between effluent and non-effluent paddocks of either property. Given a high degree of soil Cd variability that was evident between paddocks of common soil type and management history, where significant soil Cd enrichment has occurred it is recommended that all paddocks should be tested independently so as quantify soil Cd variability within individual land management units. Results should then be weighted on proportional land area and summed to provide a weighted property-mean soil Cd concentration. This will provide the most reliable representation of the property-mean soil Cd concentration when assessed under the Tiered Fertiliser Management System. In addition, it will also enable zones to be identified where there is greater risk of plant / animal Cd accumulation, where remediation or alternative management may be appropriate.

3.2 Introduction

Cadmium (Cd) accumulation in New Zealand agricultural soils driven by incidental Cd input through P fertiliser application has been well documented (Bramley, 1990; Roberts *et al.*, 1994; Bolan, 1996; Loganathan *et al.*, 2003). Initial steps to manage Cd accumulation were implemented by the New Zealand fertiliser industry in the form of self-regulation on Cd concentration in P fertilisers marketed in New Zealand. Over the period 1995-1997, the maximum permissible Cd concentration in P fertiliser was progressively decreased from historic levels averaging approximately 550 mg Cd kg^{-1} P (Rothbaum *et al.*, 1986; Roberts *et al.*, 1994; McDowell, 2012) to the current maximum of 280 mg Cd kg^{-1} P (MAF, 2008; Rys, 2011). This resulted in the phasing out of high-Cd Nauru and Christmas Island phosphate rocks that historically were the primary rocks used for superphosphate manufacture in New Zealand (Bramley, 1990; Loganathan *et al.*, 1995; McLaughlin *et al.*, 1996; Loganathan *et al.*, 2003).

However, amid on-going concerns regarding historic and on-going soil Cd accumulation (Kim, 2005) a new National Cadmium Management Strategy (NCMS) was implemented, which included the adoption of a Tiered Fertiliser Management System (TFMS) for managing on-going soil Cd accumulation in agricultural land (MAF, 2011; Cavanagh, 2012). Further to this, Cd was recently included in a new set of soil contaminant standards under the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health (NES) (MfE, 2011). Although agricultural land is exempt from the NES, it has potential to affect land use flexibility and value. For example, conversion of agricultural land to rural-residential land use triggers a requirement for contaminated land assessment, under which the soil contaminant standard for Cd is 0.8 mg kg^{-1} (MfE, 2011), which is well within the range of soil Cd concentrations reported for New Zealand agricultural soils (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b).

As a consequence of the implementation of the TFMS and NES, there is renewed focus on assessment of soil Cd concentrations in agricultural land. To provide a consistent standard for the assessment of soil Cd concentrations under the TFMS, the Fertiliser Association of New Zealand (FANZ) has developed a recommended soil sampling protocol (FANZ, 2016). This is briefly summarised in Table 3.1 below.

Table 3.1. Summary of the FANZ-recommended soil sampling protocol for soil Cd assessment under the TFMS (FANZ, 2016).

- Farms to be sampled should be selected on the basis of their phosphate fertiliser history, targeting those with a history of receiving greater than 30 kg P/ha/year
- Initial 'screening' of soil Cd concentrations can be carried out using standard 0-75 mm soil samples used for routine soil analysis. However, for 'definitive' soil Cd assessment, the following protocols should be followed:
    - Farms should be divided in to land management units (LMUs; typically up to 2-3 per farm) based on paddocks of similar management history and soil type
    - Samples should be taken from at least 6 monitor paddocks within each LMU. Ensure the monitor paddocks are well spread around the land management area the group covers. These samples can be analysed independently or aggregated into a single sample per LMU for analysis
    - When monitor paddocks within a LMU are analysed independently, the mean soil Cd concentration for the LMU is the correct value to use
    - 15-20 cores (0-150 mm depth) should be taken from a transect (or grid) placed in a representative area of the monitor paddock
    - LMU groups with very small numbers of paddocks should be avoided, by 'tying' these paddocks into other LMU groups
    - When soil Cd concentrations are approaching TFMS soil Cd trigger values, testing all individual paddocks is advised

Within the pastoral sector, soil Cd has been shown to be particularly enriched under long-term dairy land use (Taylor *et al.*, 2007; McDowell *et al.*, 2013; Cavanagh, 2014b). These farms are therefore likely to be most affected by new management criteria or restrictions imposed through application of either the TFMS or NES. Currently, there is no published information available regarding the variability of soil Cd within long-term dairy farm systems. This data is essential for underpinning the development and application of robust on-farm strategies for managing soil Cd under the TFMS or NES.

This chapter is therefore focused on providing this new knowledge. Firstly, for the purpose of informing a reliable and defensible methodology for the assessment of soil Cd within an individual farming property. Secondly, the detailed soil survey and spatial variability analysis undertaken within these properties will provide the basis for identifying suitable soils and sites

for subsequent pot and field trials carried out within the broader research initiative of this thesis.

3.3 Case study farm descriptions

Two case study dairy farms, located in the Waikato and Canterbury regions, were used to understand factors influencing soil Cd spatial and depth variability. These farms were chosen based on their long history under dairy land use, the availability of detailed farm and fertiliser records, and the existence of strongly contrasting soil types both within and between the two properties. Summaries of both of these properties are provided in the sections below.

3.3.1 Waikato farm

3.3.1.1 General management history

Located approximately 10 km southeast of Morrinsville (37°41'52.1"S 175°37'26.9"E), the total effective area of this property is 81 ha. The property consists of two main units (Figure 3.1); the original family-owned farm to the west (46 ha effective) and a newer block (35 ha effective) to the east that was purchased in 2001. This eastern block was used for dairy production by the previous owners. The property is predominantly rolling in contour (Figure 3.2) rising in elevation from 45 m to 90 m above mean sea level. There has been little soil tillage history with very little cropping or pasture renewal being undertaken. Through a single milking shed, 140 mixed-age cows are milked twice-a-day on the original home block, and a further 90 cows being milked once-a-day on the new block. All stock including replacements are retained on-farm all year round, with replacements rotationally grazed around the entire property. No paddocks within the property have historically been strategically allocated for ‘night’ or ‘day’ grazing of the milking herd, a management factor that can contribute to contrasting excreta return loading (Goodall, 1951).

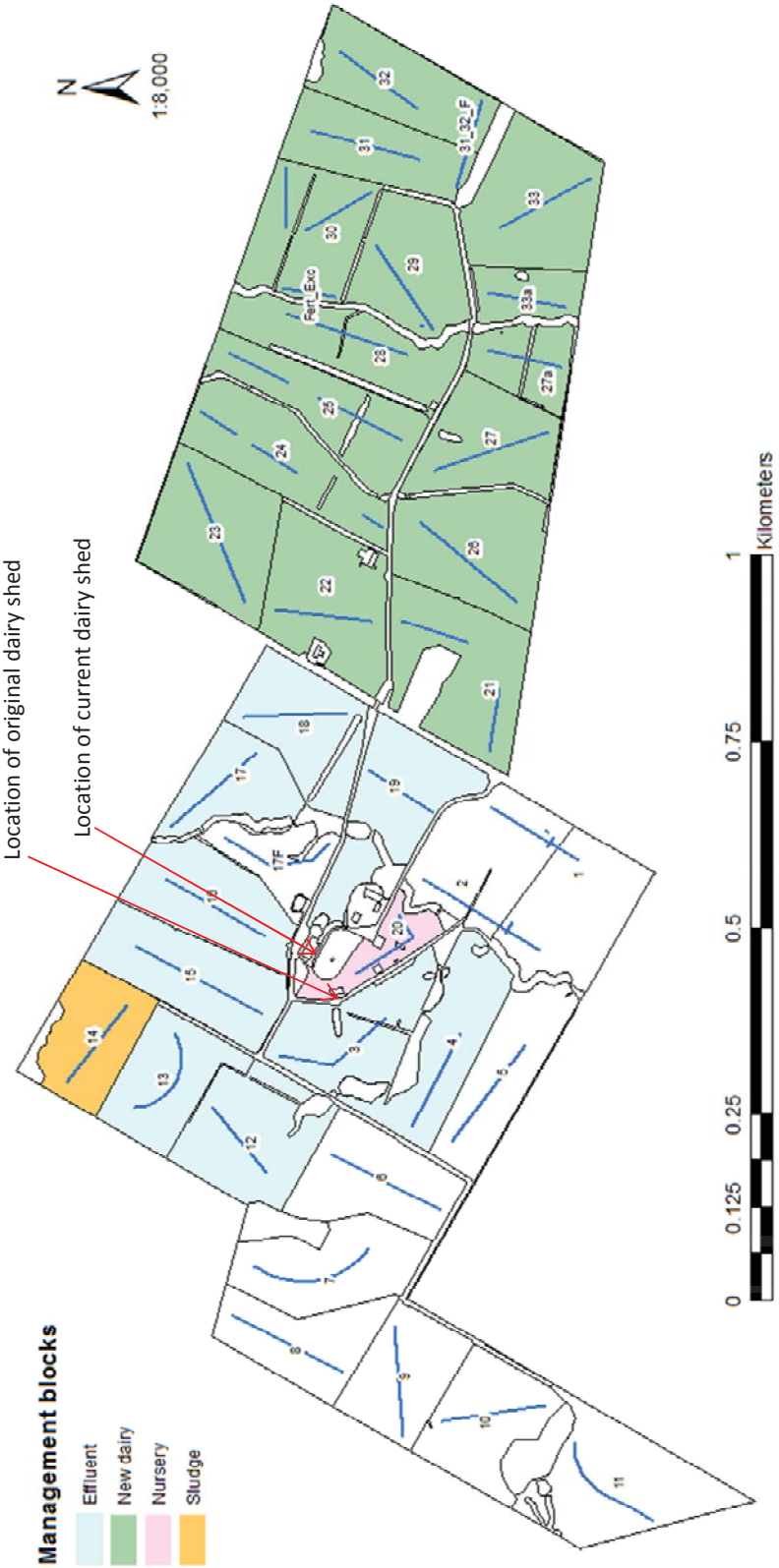

Figure 3.1. Farm map for the Waikato property showing management blocks and 'all-paddock testing' soil testing transects (numbered blue lines).

Figure 3.2. Farm map for Waikato property showing slope classes derived from the digital elevation model, 5m contour lines and 'all-paddock testing' soil testing transects (numbered blue lines).

3.3.1.2 Effluent and P fertiliser management

Historically, raw effluent was applied directly from a sump at the dairy shed to paddocks 3 and 4 (Figure 3.1). A non-agitated effluent holding pond was installed in 1998, with liquid effluent being applied to paddocks 12, 13, 15-19 (16 ha total area). Settled solids are removed from the effluent holding pond annually and applied to paddock 14 (2 ha).

The property has traditionally had a rich history of P fertiliser inputs, with superphosphate being the predominant P fertiliser applied. Records from 1995 to 2001 indicate an average annual application rate of 55 kg P ha^{-1}, although no records exist prior to this time. Over the period 2001-2013 this reduced to an average annual application rate of approximately 21 kg P ha^{-1}. This lower application rate was a conscious decision by the owners to reduce P fertility to the target range (Olsen-P 20-30 mg L^{-1}; Roberts and Morton (2009)) since historic P fertiliser inputs had driven P fertility well in excess of this range (the average Olsen-P was approximately 55 mg L^{-1} in the early 2000's). Historically, P fertiliser has been applied uniformly across the property, regardless of landform, land use management, or soil type. The only exceptions to this are paddock 14, which has not had any P fertiliser input since 2001 (receiving only sludge from the effluent pond), and paddock 20, which is a small nursery area and has had little P fertiliser applied historically.

3.3.1.3 Soils

With assistance from Massey University staff, a detailed soil survey was undertaken to identify soil types and soil boundaries within the property. Soil survey inspection points were taken approximately every 80 m. From this data, a detailed soil map was produced (Figure 3.3). The predominant soil types on the property are the well-drained Kereone silt loam, which occupies the majority of the rolling contour of the property, and the poorly-drained Topehaehae sandy clay loam, which occupies the lower lying areas.

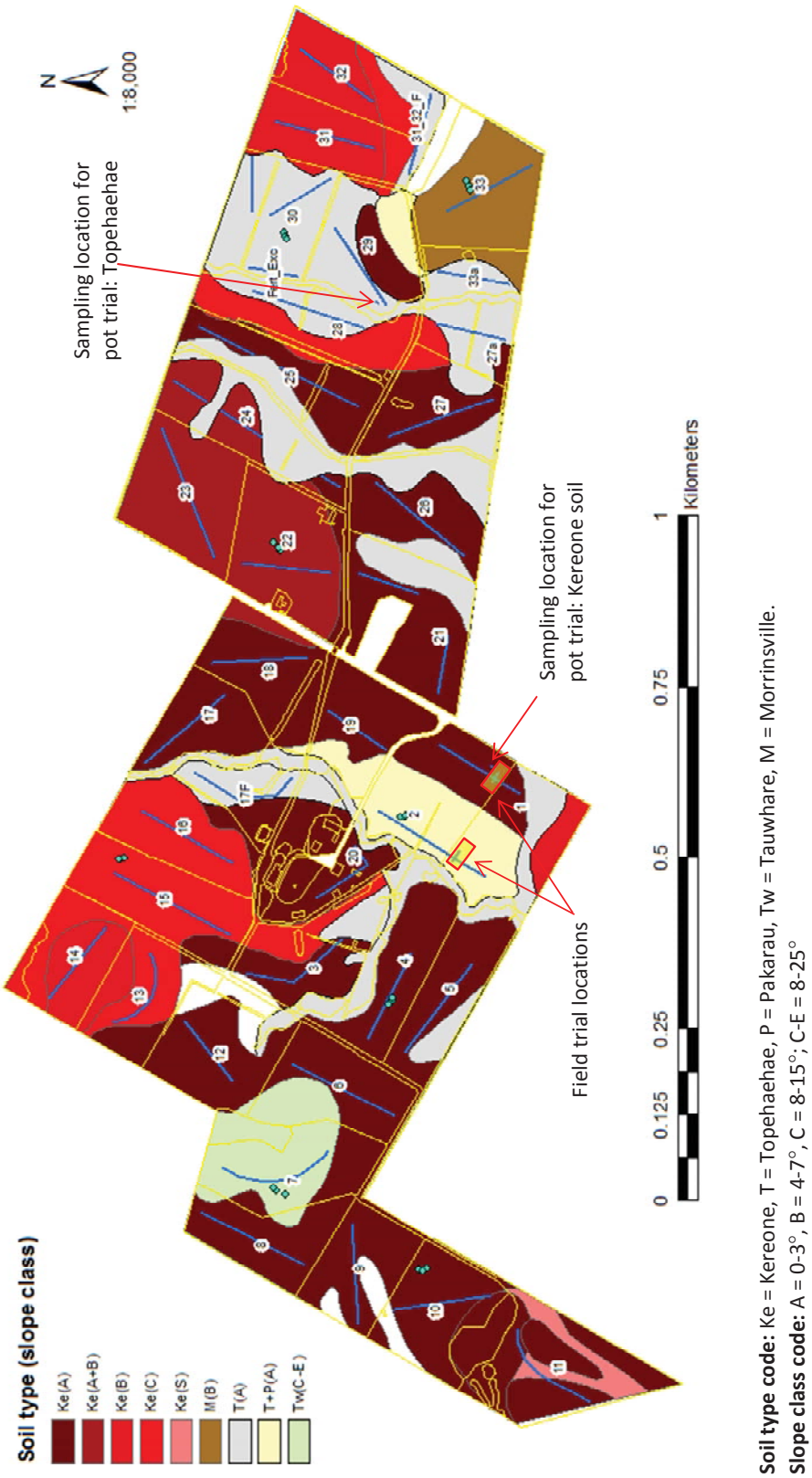

Figure 3.3. Detailed soil map for the Waikato farm. Also shown on the map are 'all-paddock testing' soil testing transects (blue lines) and sites where intact soil cores were collected for analysis (light blue circles).

Small areas of other soil types are found within the property, with all soils and their respective areas described briefly in Table 3.2. Detailed soil profile descriptions are located in Appendix 1 (Section A1.1).

Table 3.2. Summary of soil types and their respective areas within the Waikato farm.

Soil series	New Zealand Soil Classification	Drainage class	Area (ha)
Kereone silt loam	Typic Orthic Allophanic	Well drained	56.7
Morrinsville clay loam	Typic Orthic Granular	Moderately well drained	3.2
Tauwhare hill soil	Mottled Orthic Recent	Imperfectly to poorly drained	2.6
Topehaehae sandy clay loam	Typic Recent Gley	Poorly drained	15.4
Topehaehae sandy clay loam interspersed with Pakarau silt loam	Typic Recent Gley Typic Orthic Allophanic	Poorly drained to Moderately well drained	3.4
		Total	*81.3*

3.3.2 Canterbury farm

3.3.2.1 General management history

Located southwest of Lincoln (43°39'11.6"S 172°28'11.1"E) within the Canterbury plains, this family farm has been in dairying land use since the 1960's. The original milking platform (80 ha) consisted of paddocks 1-13 & 18-32 (Figure 3.4). Originally, approximately 160-180 cows were milked on this area under a winter milk programme, although numbers were gradually built up to reach approximately 320 cows during the 1990's to 2004. During this period, hay was traditionally harvested from paddocks 1-3 & 7-9, while paddocks 29-31 were also used for silage during the late 1980's to the late 1990's. The western part of the property (paddocks 43-49, 40 ha; Figure 3.4) was traditionally used as a support block, being sown in winter forage brassica crops and barley, as well as being used for grazing of replacement stock and beef animals. These paddocks are now incorporated into the current expanded milking platform, although due to the distance from the milking shed, paddocks 47-49 tend to be used for grazing of milking herd replacement stock from around 9 months of age. A new, undeveloped block to the south east (paddocks 14-17, 30 ha; Figure 3.4) was purchased in 2004. Under the previous owner, this land area had been used mainly for cereal cropping and provision of conserved feed (hay).

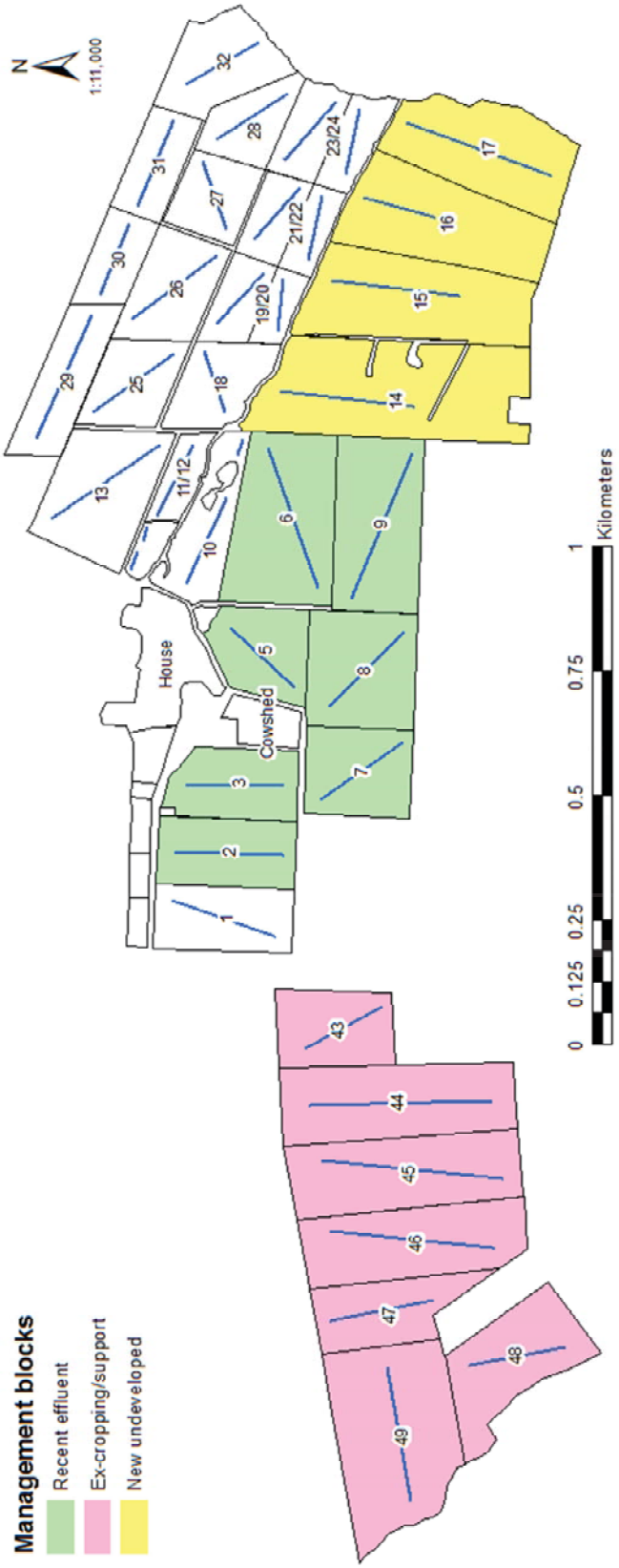

Figure 3.4. Farm map for the Canterbury property showing management blocks and 'all-paddock testing' soil testing transects (numbered blue lines).

The total effective area of the current milking platform is 152 ha. Upon this, approximately 500 cows are milked at peak, although all cows are wintered off the property during June and July. With the growth of the dairy platform, a new rotary milking shed was installed in 2004 (occupying what was originally paddock 4; Figure 3.4) to cater for the larger number of dairy cows being run on the property. To provide additional supplementary feed for the dairy cattle, barley grain and compressed barley/protein feed pellets (100 and 150 tonne dry weight/year, respectively) is imported and provided to stock via an in-shed feeding system. In addition, around 500 tonne silage (dry matter basis) is harvested on the property, predominantly from the effluent block as well as paddocks 47-49. Contrasting the Waikato dairy farm, this property has regularly undergone cultivation through rotational pasture renewal and/or cropping.

3.3.2.2 Effluent and P fertiliser management

Effluent has been irrigated to land direct from a sump at the milking shed since the rotary shed was installed in 2004. Effluent is applied to paddocks 2, 3, 5-9 (32 ha total), with paddock 9 tending to receive more regular and greater effluent inputs (Figure 3.4).

Up until the 1990's this farm received only light rates of P fertiliser, typically receiving 250 kg ha^{-1} of 20% potash superphosphate annually (18 kg P ha^{-1} y^{-1}). During the 1990's and 2000's, higher rates of P fertiliser were applied to increase soil P fertility, with typical P fertiliser inputs in recent years being around 35 kg P ha^{-1} predominantly as superphosphate-based products. On blocks receiving dairy shed effluent, only 12 kg P ha^{-1} is applied as P fertiliser in recognition of the P inputs in the effluent.

3.3.2.3 Soils

A detailed soil survey was carried out, allowing a property-specific soil map to be generated (Figure 3.5). Located on a flat alluvial plain, the soils of this property are predominantly deep, fine-textured, imperfectly and/or poorly drained Pallic and Gley soils.

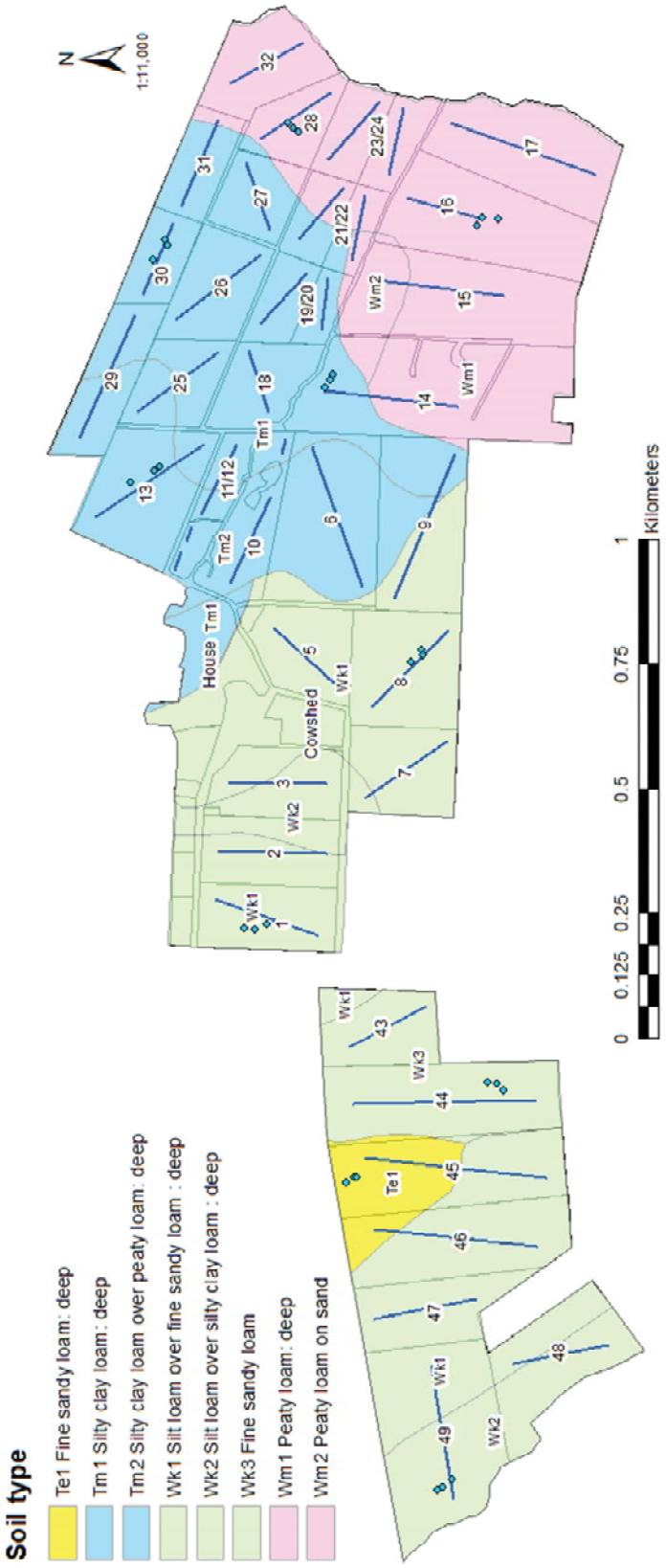

Figure 3.5. Detailed soil map for the Canterbury farm. Also shown on the map are 'all-paddock testing' soil testing transects used for assessing soil Cd concentrations within the property (blue lines) and sites where intact soil cores were collected for analysis (light blue circles).

The soil types and variants, along with their respective areas are briefly summarised in Table 3.3, with more detailed soil profile descriptions provided in Appendix 1 (Section A1.2).

Table 3.3. Summary of soil types and their respective areas within the Canterbury farm.

Soil series	New Zealand Soil Classification	Drainage class	Area (ha)
Templeton fine sandy loam (Te1)	Typic Immature Pallic	Well drained	4.6
Temuka			
- silty clay loam (Tm1)	Typic Orthic Gley	Poorly drained	26.2
- silty clay loam over peaty loam (Tm2)			18.0
Wakanui			
- silt loam over fine sandy loam (Wk1)	Mottled Immature Pallic	Imperfectly drained	42.1
- silt loam over silty clay loam (Wk2)			12.3
- fine sandy loam (Wk3)			9.8
Waimairi			
- peaty loam (Wm1)	Peaty Orthic Gley	Poorly drained	36.1
- peaty loam on sand (Wm2)			2.8
		Total	*152*

3.4 Methodology

3.4.1 Inter-paddock variability

In both properties, all-paddock soil testing (APT) was initially undertaken to explore soil Cd variability and relationships to other soil properties. In most paddocks, a single soil testing transect was established, positioned to best represent the landform and predominant soil type within the paddock, while minimising likely sources of variability (e.g. fences, troughs etc.). Where obvious, soil testing transects were located to avoid changes in soil type, although this was difficult in the case of the Canterbury farm where soil type variations were subtle, with intergrades between soil types and indistinct soil boundaries. In the Waikato farm, where some paddocks contained large areas of strongly contrasting soil types, more than one transect was established to independently represent these within-paddock soil type variations (i.e. transect 1 and 2, transect 17 and 17F, transect 31, 32 and 31_32_F). All transects were marked by global positioning system (GPS) location, using a handheld Garmin GPS72.

Fifteen soil cores (25 mm diameter, 150 mm deep) were collected along the length of each transect, with individual cores spaced at regular intervals (typically every 10 m, but dependent on the overall length of the transect). Upon collection, each soil core was split into 0-75 mm

and 75-150 mm subsections, using an improvised device to ensure consistency (Figure 3.6). These subsections were then aggregated independently for analysis, such that each transect was represented by two samples (0-75 mm and 75-150 mm soil core depths). In total, 38 transects (samples) were independently analysed within the Waikato farm, while 34 transects were analysed within the Canterbury farm. Total Cd was analysed at both soil depths, however, only the 0-75 mm soil samples were analysed for general soil properties (total P, Olsen-P, total C, total N, P retention, CEC and pH).

Figure 3.6. Improvised soil core sectioning device used to separate 0-75 mm and 75-150 mm sub-samples (photograph courtesy of the author).

3.4.2 Intact soil cores

Guided by the detailed soil maps created from the soil survey, intact soil cores were collected from pre-determined sites within each property, each representing differences in soil type and/or land management history. In total, 8 sites were sampled within the Waikato farm (locations shown in Figure 3.3), while 10 sites were sampled within the Canterbury farm (locations shown in Figure 3.5). These intact cores were collected to a depth of 400-600 mm, with 3 replicates being taken in close proximity (~10 m) at each sampling site. Maximum core depth was limited in some soils by the ability to retrieve cores intact and with minimal

disturbance. To retrieve the intact soil cores, a steel tubular corer (46 mm internal diameter, with slightly narrower cutting tip to allow easier core retrieval) was driven into the soil using a Waratah (Y-post) driver (Figure 3.7.a). Cores were gently pushed back out of the corer into PVC tubes (Figure 3.7.b) which were then sealed for transport, minimising risk of disturbance prior to analysis (necessary for spectral analysis related to research reported in Chapter 6).

Figure 3.7.a) Device used to collect intact soil cores from the field, and **b)** Example of intact soil core (still inside the corer) and adjacent PVC pipe used to transport the intact cores (photographs courtesy of Michael Hedley).

3.4.3 Intra-paddock soil Cd variability testing

Intensive soil sampling was carried out in two paddocks within the Waikato dairy farm (paddocks 6 and 18, Figure 3.1) to collect data on intra-paddock soil total Cd concentration variability. In both paddocks, 26 samples (5 soil cores per sample, to 150 mm depth) were collected for independent assessment, with GPS references taken at each location. Due to inherent limitations of handheld GPS accuracy, measurements were also taken within paddock to provide physical references points for individual rows of samples).

In paddock 18, a 36 x 26 m rectangular grid was used (4 rows of 5 samples and 1 row of 6) within the entire paddock area north of a row of trees located towards the southern end of the paddock (Figure 3.8.a). The contour of this paddock was relatively consistent, with a gentle gradient towards higher altitude at the northern end of the paddock. In paddock 6, intensive soil sampling was focussed into the north-western area of the paddock (Figure 3.8.b). Focus was placed within this area since there was a combination of landscape features that were of interest for potential influence on soil Cd spatial variability. In particular, this zone encapsulated a transition from steep grazed slopes in paddock 7 (immediately to the west) to relatively flat, even contour towards the centre and east of paddock 6. Further to this, a native bush area had been fenced off in a natural spring-seepage area at the toe-slope of paddock 7 adjacent to the north western boundary of paddock 6. Soil samples were collected with greater intensity (every 11 m) along the western boundary of paddock 6, since greater variation in slope / vegetation factors in that zone was thought likely to generate the most variable soil Cd concentrations. The remainder of samples were taken in three rows with samples spaced 20 meters apart.

Figure 3.8. Soil sampling patterns used for intra-paddock soil Cd variability assessment in **a)** paddock 18, and **b)** paddock 6. Five metre contour lines are shown for topographic reference.

3.4.4 Soil analysis

3.4.4.1 Total Cd

Analysis of soil samples was carried out at Hill Laboratories (Clyde Street, Hamilton). Soil samples were oven-dried at 38°C for a minimum of 16 hours, before being crushed and sieved (< 2 mm). Based on the USEPA methodology of Martin *et al.* (1994) soil 'pseudo'-total Cd (hereafter referred to as total Cd) analysis was undertaken by digesting 0.5 g of soil in 1 mL of concentrated nitric acid, 1 mL of concentrated hydrochloric acid, and 5 mL of deionised water, for 2 hours at 120°C. Once cooled, digests were made up to 20 mL with deionised water before centrifuging for 5 minutes at 2000 rpm. Aliquots of the digest solution were then diluted 10-fold with 5% nitric acid, before analysis for Cd using a Perkin-Elmer NEXION 300D Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS). The limit of detection (LOD) for Cd using this methodology was 0.02 mg kg^{-1}. For quality control purpose, two blanks and one standard reference material (Australian Government Analytical Laboratories (AGAL) 10; Hawkesbury River sediment) were included within every batch of 40 samples. The working-limit Cd recovery range for the standard reference material was 93-105% (F. Calvert, personal communication, September 28, 2016). Calibration rescale was performed every 20 samples to correct for instrument drift.

3.4.4.2 Total P

Soil digests used for total Cd analysis were also analysed for total P. The only difference was in the final dilution prior to analysis, where aliquots of digest solution for total P analysis were diluted 5-fold with deionised water. Analysis for total P was carried out using a Thermo Scientific iCAP 6500 Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES). The LOD for total P using this methodology was 65 mg kg^{-1}.

3.4.4.3 Total organic carbon and nitrogen

Total organic carbon and nitrogen (hereafter referred to as total C and total N) was analysed using an Elementar VARIO MAX Cube. No acid pre-treatment was used, since despite the possibility of lime residues, the calculated inorganic C (carbonate) contribution from these residues was determined to be insignificant (<5% of the soil organic C concentrations expected). Dried and ground soil samples (0.13 g) were wrapped in aluminium foil along with tungsten as a combustion activation catalyst. These samples were then combusted in an oxygen stream at 900°C. After passing through a reduction chamber containing copper oxide, the size and timing of volatile flow peaks (N_2 and CO_2) were assessed via a thermal conductivity detector. The LOD for total C and N using this technique was 0.1% and 0.04%, respectively.

3.4.4.4 Plant available P (Olsen-P)

Plant available phosphorus was analysed based on the Olsen-P technique described by Blakemore *et al.* (1987). Briefly, dried and ground soil subsamples (5 mL) were shaken end-over-end for 30 minutes in 100 mL of 0.5 M sodium bicarbonate (pH 8.5). Phosphorus in the extract solution was then determined colourmetrically using the molybdenum blue technique of Murphy and Riley (1962). Absorbance at a wavelength of 880 ηm was assessed using a Lachat 8500 Series 1 Flow Injection Analyser. The LOD using this methodology was 1 mg L^{-1}.

3.4.4.5 Soil pH

Soil pH analysis was based on the methodology of Blakemore *et al.* (1987), whereby 20 mL of deionised water was added to 10 mL of ground, air-dried soil (providing a 1:2 (v/v) soil to water slurry), which was then left to stand overnight. Without stirring, solution pH was measured the following day using a Thermo Scientific Orion ROSS Sureflow pH electrode coupled with a ManTech AutoMax robotic sampler. The LOD using this technique was 0.1 pH units.

3.4.4.6 Phosphate retention (P retention)

Based on the methodology of Blakemore *et al.* (1987), soil subsamples (4 g) were extracted over 16 hours in 20 mL of 1000 mg L^{-1} P solution (buffered to pH 4.65), before filtering (Sartorius No. 292). Phosphorus remaining in solution was determined colourimetrically (using nitric vanadomolybdate reagent) on an Aquakem 250 discrete analyser, with absorbance measured at 420 ηm. Phosphorus retained by the soil was calculated by the difference in concentration compared to the original buffer solution, and expressed as a percentage. The LOD using this technique was 3%.

3.4.4.7 Cation exchange capacity (CEC)

Soil samples (3 mL) were extracted for 30 minutes in 60 mL of 1 M ammonium acetate that had been adjusted to pH 7, then filtered (Sartorius No. 389). Cations in the extracts were measured using a Thermo Scientific iCAP 6500 ICP-OES. Extractable acidity was calculated by the decrease in pH of the original pH-buffered ammonium acetate solution, determined using a Thermo Scientific Orion ROSS Sureflow pH electrode. CEC was then calculated as the sum of extractable cations and the extractable acidity. The LOD was 2 meq 100 g^{-1} soil.

3.4.5 Statistical analysis

Statistical analysis was carried out using the software SPSS (IBM Corp, 2013). Analysis of variance (ANOVA) tests were undertaken to identify whether significant differences existed between treatments overall. Tukeys honestly significant difference (HSD) was run as a post-hoc analysis to identify differences between individual treatment means. Spearman's rank-order technique was used to determine the correlation between soil total Cd and other soil variables. Linear regression analysis was also performed to describe the relationship between soil total Cd measured at 0-75 and 0-150 mm sampling depths, as well as the relationship between soil total Cd and total P or Olsen-P. Esri® ArcMap™ (version 10.3) Geographic Information System (GIS) software was used to map both properties and to undertake

statistical interpolation (spherical semivariogram kriging, using all data points and a variable radius) of soil Cd concentrations determined within the intra-paddock soil Cd variability assessment. Discrete polygon analysis was also used to calculate the area of different soil types within individual paddocks or land management units.

3.5 Results

3.5.1 Waikato farm

3.5.1.1 Spatial variability in soil Cd concentrations

Large variation in soil total Cd concentrations was evident within this property. At the standard soil fertility assessment sampling depth of 0-75 mm (typically used for soil Cd property-screening purposes under the TFMS (FANZ, 2016)) the mean soil total Cd concentration was 1.27 mg kg^{-1}, with a range of 0.64-1.88 mg kg^{-1} (Figure 3.9).

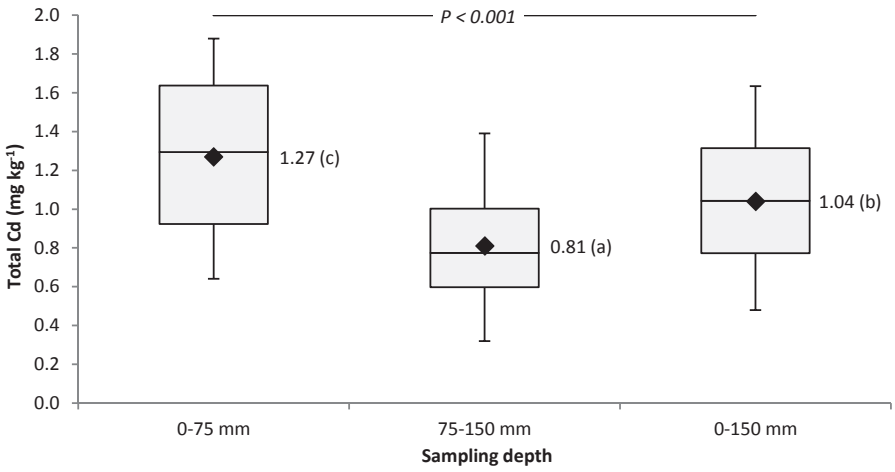

Figure 3.9. Range in soil total Cd concentrations within the Waikato farm for sampling depths of 0-75, 75-150 and 0-150 mm. Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* value provided for comparison of means. Letters in brackets indicate where means are significantly different ($P < 0.05$).

At the TFMS 'definitive' sampling depth of 0-150 mm (FANZ, 2016) the mean soil total Cd concentration was 1.04 mg kg^{-1}, with a range of 0.48-1.64 mg kg^{-1} (Figure 3.9). The mean soil Cd concentration at 0-150 mm depth therefore represented 82% of that at 0-75 mm depth,

with this difference being significant ($P < 0.05$). The lower soil Cd concentrations at 0-150 mm sampling depth was a consequence of dilution, due to significantly ($P < 0.05$) lower soil Cd concentrations occurring in the 75-150 mm depth range (mean 0.81 mg kg^{-1}, range 0.32-1.39 mg kg^{-1}).

Significant ($P < 0.001$) relationships existed between soil total Cd and the soil variables total P, total C, total N, P retention and CEC, with total P having the strongest correlation (Spearman's *rho* = 0.923) to total Cd concentration (Table 3.4). There was no relationship ($P = 0.953$) between soil total Cd and Olsen-P.

Table 3.4. Spearman coefficient of correlation and significance between soil total Cd and various soil parameters within the Waikato farm (0-75 mm sampling depth, $n = 38$).

	Total P	Olsen-P	Total C	Total N	P retention	CEC
Correlation coefficient	0.923	-0.010	0.864	0.840	0.831	0.884
P value	*<0.001*	*0.953*	*<0.001*	*<0.001*	*<0.001*	*<0.001*

Paddock-level spatial variation in soil total Cd and total P concentration is shown in Figure 3.10 and Figure 3.11, respectively. Due to the strong correlation between total Cd and total P (Table 3.4), similar spatial variability patterns were observed for these soil parameters.

3.5.1.1.1 Effect of soil type on soil Cd concentration

Direct comparison of the predominant two soil types within the property (Kereone and Topehaehae) indicated that soil Cd concentrations were significantly ($P < 0.001$) greater in the Kereone than the Topehaehae soil (Figure 3.12). Due to very limited representation within the property, the Topehaehae+Pakarau, Morrinsville and Tauwhare soils were only assessed by one transect each, and for this reason they were not included within the statistical analysis.

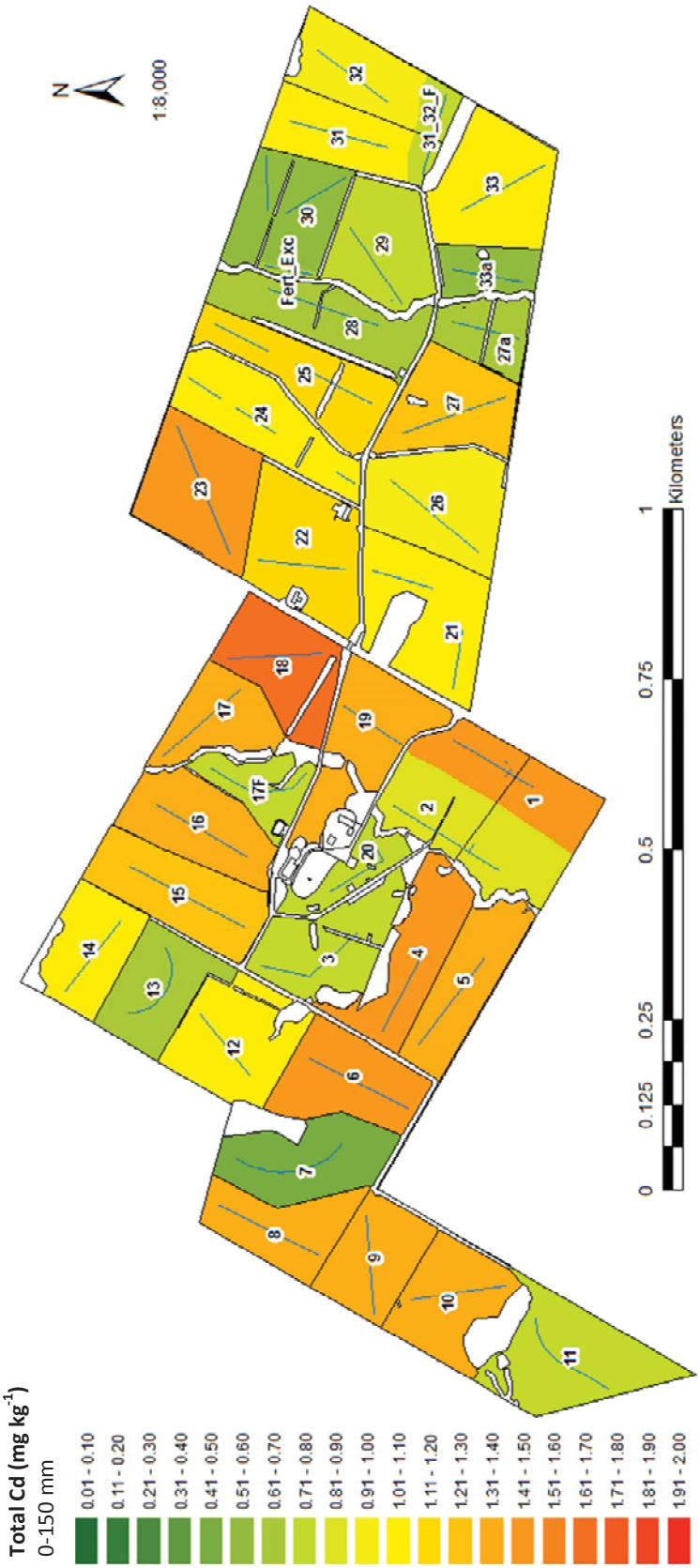

Figure 3.10. Inter-paddock soil total Cd (mg kg^{-1}) variability within the Waikato farm (0-150 mm sampling depth).

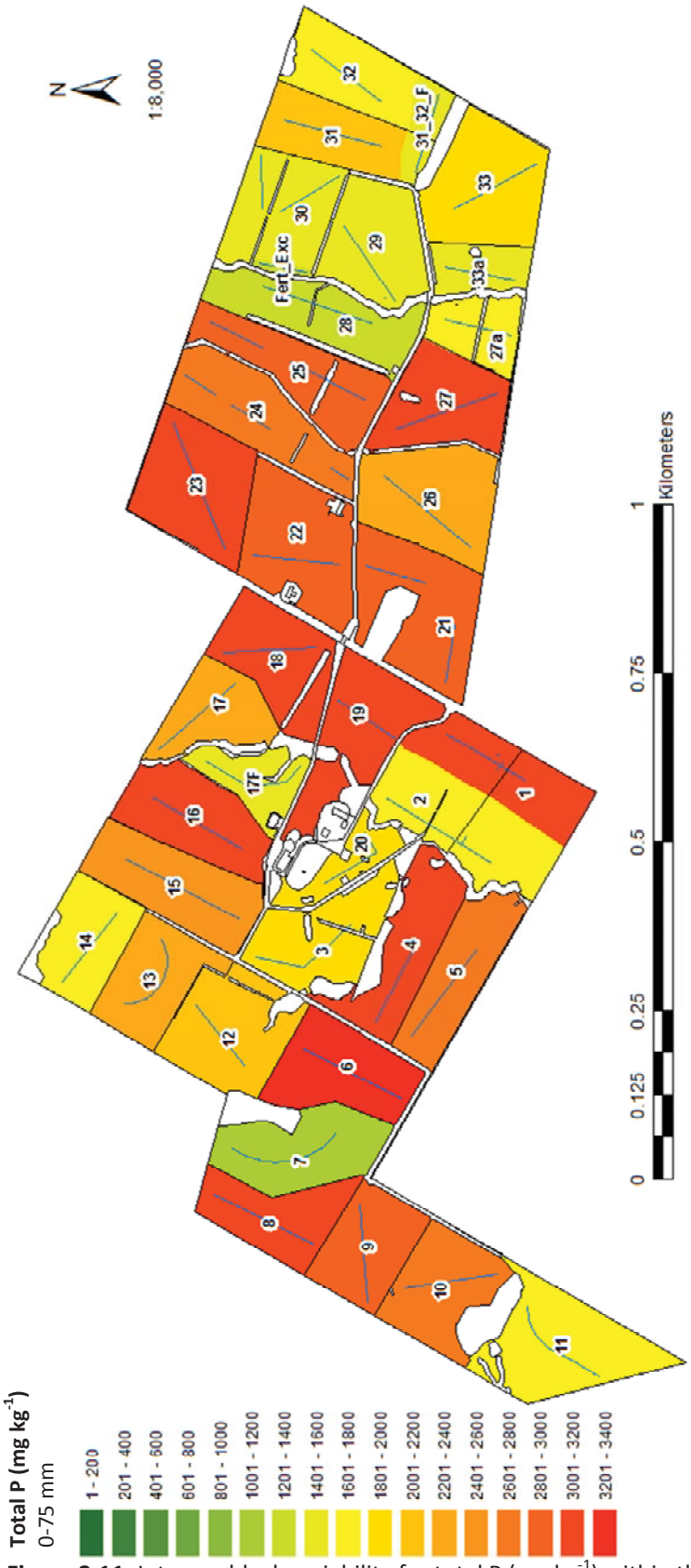

Figure 3.11. Inter-paddock variability for total P (mg kg^{-1}) within the Waikato farm (0-75 mm sampling depth).

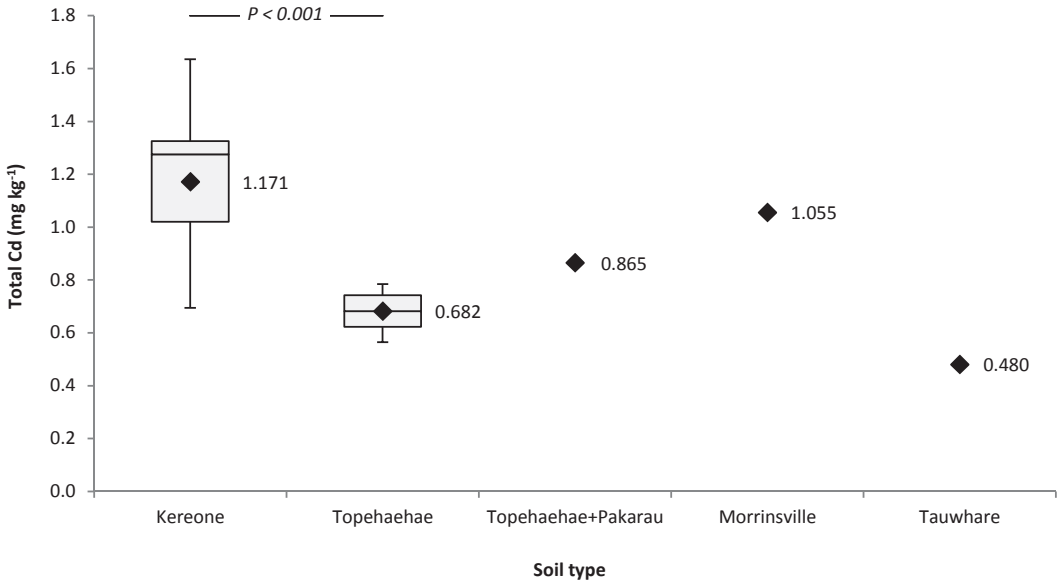

Figure 3.12. Range in soil total Cd concentrations for each soil type within the Waikato farm (0-150 mm sampling depth). Box and whisker plots represent data quartiles, black diamond and associated value is the mean (except for soils only represented by one transect). ANOVA *P* values provided for comparison of means for the predominant Kereone and Topehaehae soils.

3.5.1.1.2 Effect of slope on soil Cd concentration

The effect of slope (Figure 3.2) on soil Cd concentration is seen for transects 7, 11 and 13 (Figure 3.10), which all display low soil total Cd concentrations. Transect 7 (Tauwhare hill soil) represents the steepest contour (approximately 15-25°) within the property and also the lowest soil Cd concentration (0.48 mg kg^{-1}, Figure 3.12). Transects 11 and 13 (both Kereone soil) also returned much lower soil Cd concentrations (0.80 and 0.70 mg kg^{-1}, respectively) relative to transects on surrounding Kereone soils. In both cases, sampling transects were placed mid-slope on land that was atypically steep (approximately 15°, Figure 3.2) relative to the majority of transects representing Kereone soils (Figure 3.3). Aside from these atypically steep transects, analysis of soil testing transects for the Kereone soil type (the only soil type to have multiple slope class variations independently sampled) revealed that there was no significant difference *(P* = 0.491) in soil Cd concentrations between slope classes (Figure 3.13).

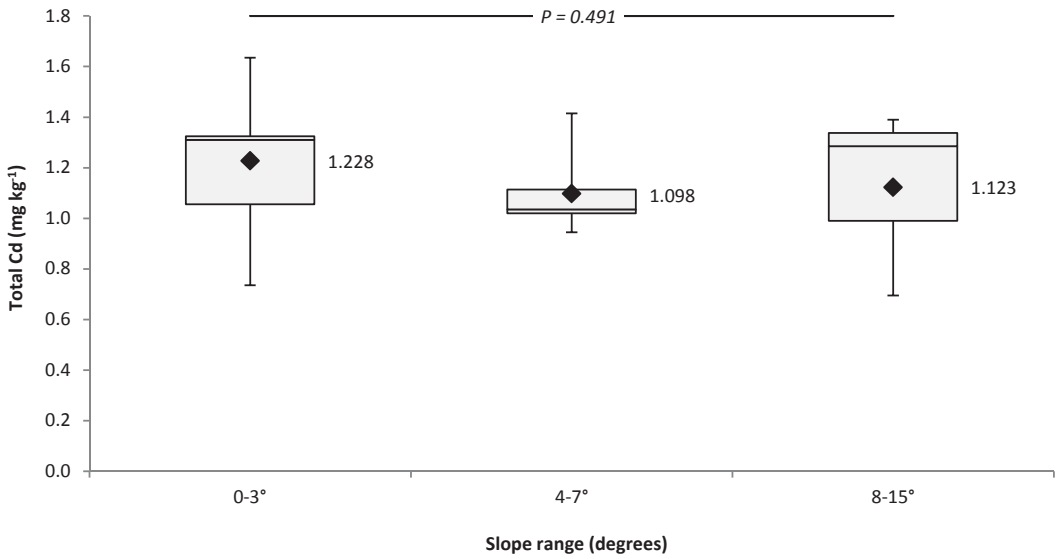

Figure 3.13. Range in soil total Cd concentrations for different slope classes within the Kereone soil type (0-150 mm sampling depth). Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* value provided for comparison of means.

3.5.1.1.3 Effect of land management history within soil types

Given the significant effect of soil type on soil Cd concentration, the effect of land management history on soil total Cd concentrations was assessed within soil type. Within this analysis, the low Cd concentrations for transects 11 and 13 were omitted as atypical 'outlier' values based on their slope anomalies. Using this approach, the range in soil Cd concentrations within each 'land management history by soil type' grouping is shown in Figure 3.14.

Within the Kereone soil type in the 'Original dairy' block, soil Cd concentrations were not significantly different ($P > 0.05$) between paddocks that had received effluent and those that had not (Figure 3.14). Soil Cd concentrations were significantly ($P < 0.05$) lower in the 'New dairy - Kereone' group than the 'Original dairy - Kereone' group, but not significantly different ($P > 0.05$) to the 'Original dairy with effluent - Kereone' group. Soil Cd concentrations in the Topehaehae soil of the 'New dairy' group were significantly ($P < 0.05$) lower than in the Kereone soils of the 'Original dairy', 'Original dairy with effluent', and 'New dairy' groups. Soil

Cd concentrations were also consistently low for isolated samples representing Topehaehae and Topehaehae+Pakarau soils within the 'Original dairy' block.

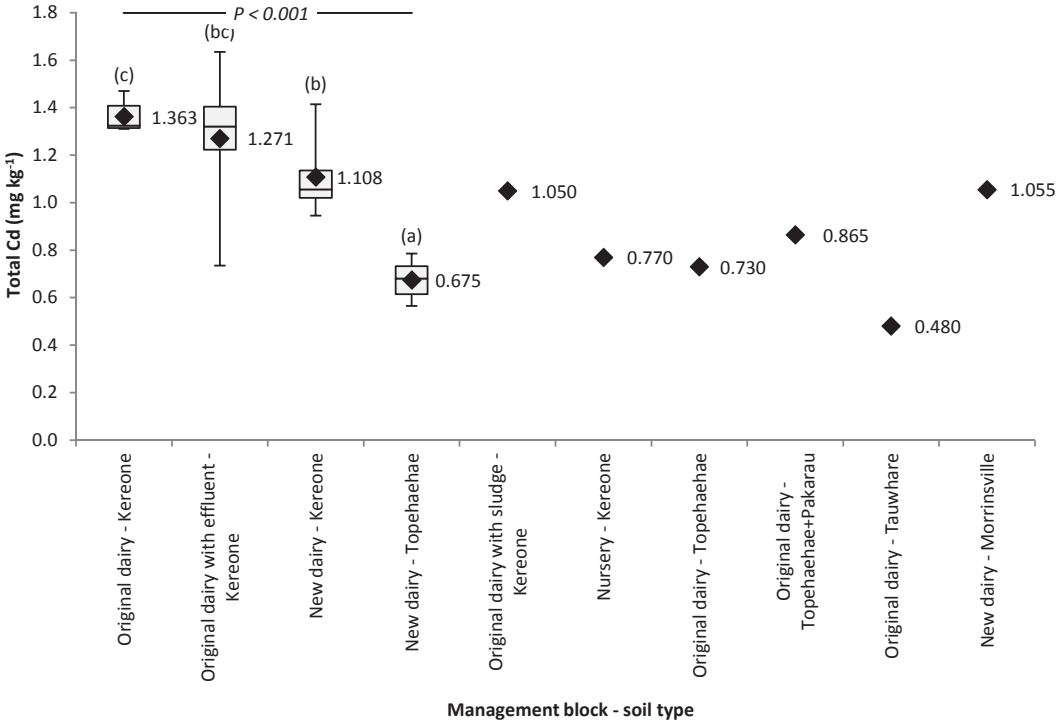

Figure 3.14. Range in soil total Cd concentrations for each land management by soil type grouping within the Waikato farm (0-150 mm sampling depth). Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* value provided for comparison of means between groups with more than 1 sample. Letters in brackets indicate where means are significantly different ($P < 0.05$).

The wide range in soil total Cd concentrations within the 'Original dairy with effluent - Kereone' group (Figure 3.14) was largely due to the atypically low value for transect 3 (Figure 3.10). This paddock is located immediately adjacent to the site of the original dairy shed (Figure 3.1) and is likely to have been used historically as a livestock holding paddock. In addition, being the closer of the original two effluent paddocks (transects 3 and 4, Figure 3.1) to the original dairy shed, it is likely to have received more frequent effluent inputs. These factors are likely to have contributed to less-frequent P fertiliser inputs to paddock 3, although this could not be confirmed by the farmer.

Soil total Cd concentrations were also atypically low in the 'Nursery' paddock (Figure 3.14). This small, irregularly-shaped paddock (transect 20, Figure 3.10) has traditionally been used as a holding paddock for young and/or unwell stock, being conveniently located adjacent to the original and current dairy sheds. As a consequence, this paddock has historically received little P fertiliser (confirmed by the farmer).

The clear linkage between P fertiliser application history and soil total Cd concentration is demonstrated by the strong correlation between total Cd and total P (R^2 = 0.84 (Figure 3.15)), with this relationship holding true across the varying soil types within the property.

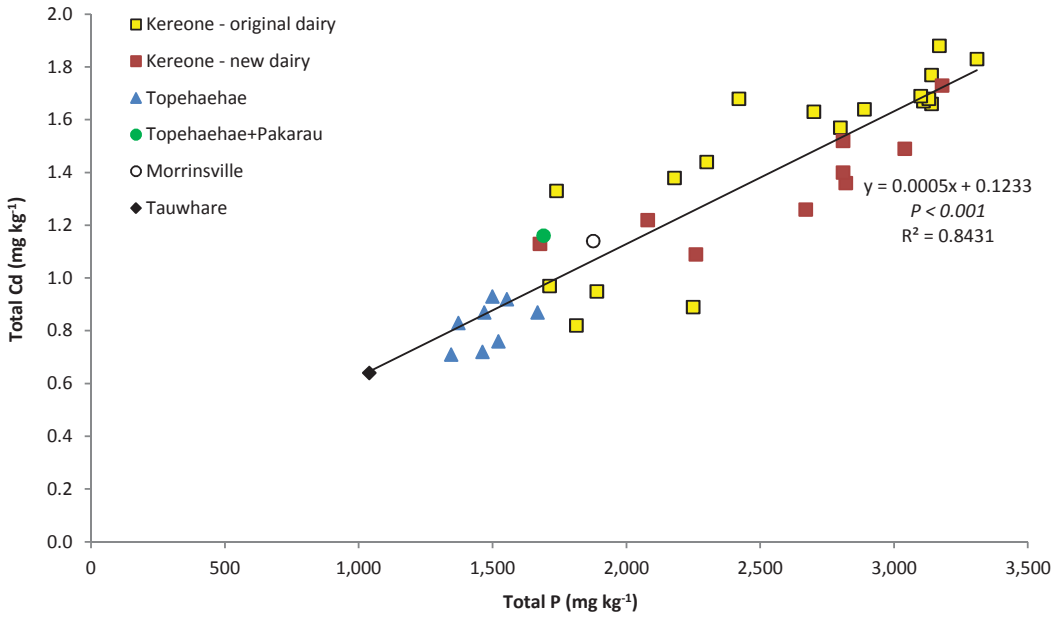

Figure 3.15. Relationship between soil total Cd and total P within the Waikato farm (0-75 mm sampling depth).

3.5.1.1.4 Intra-paddock variability (intensive soil sampling)

Soil Cd concentration gradient maps developed from intensive soil sampling are shown in Figure 3.16 (paddock 18) and Figure 3.17 (paddock 6). Within paddock 18, there was a clear gradient in soil Cd concentrations with the lowest concentrations occurring along the eastern

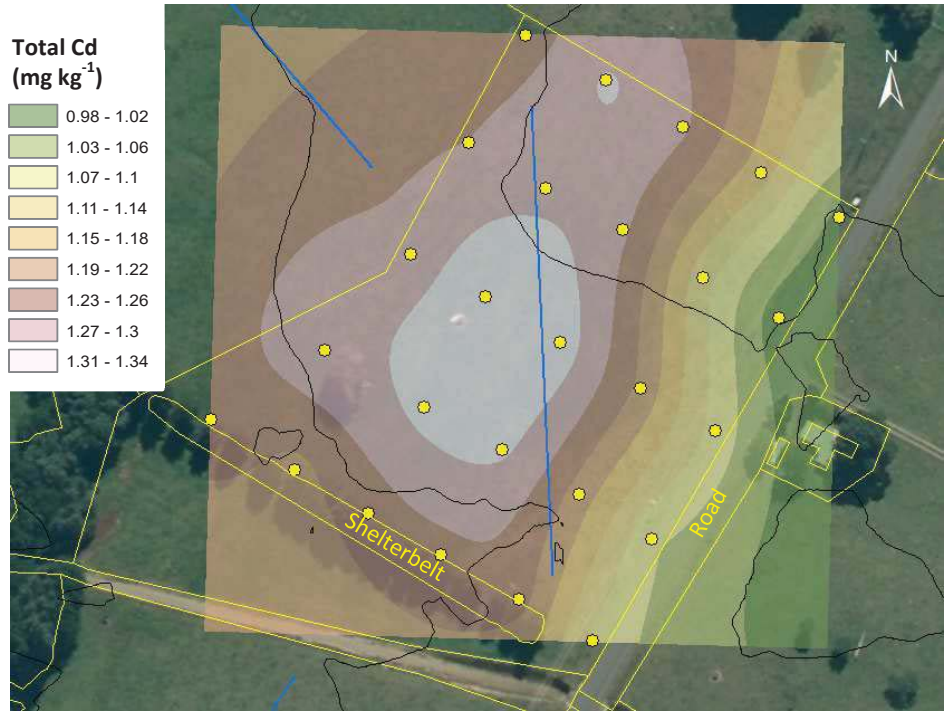

Figure 3.16. Intra-paddock variability in soil total Cd concentration (mg kg^{-1}) for paddock 18, Waikato farm (0-150 mm sampling depth). 5 m contour lines shown in black.

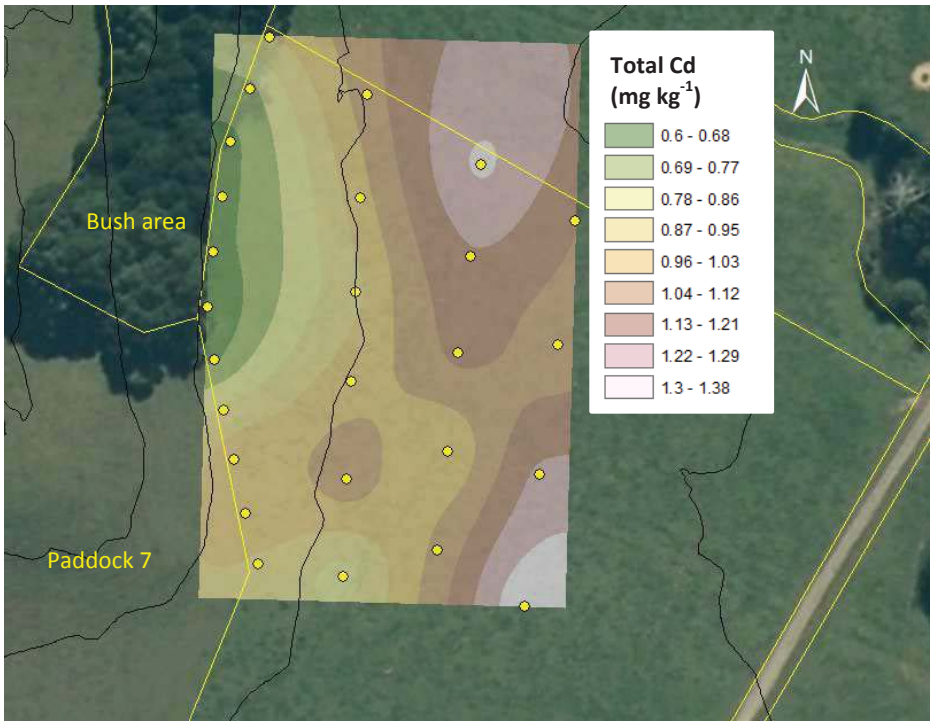

Figure 3.17. Intra-paddock variability in soil total Cd concentration (mg kg^{-1}) for paddock 6, Waikato farm (0-150 mm sampling depth). 5 m contour lines shown in black.

paddock boundary, which borders a road. The greatest Cd concentrations occurred in the central-western zone of the paddock, coinciding with the location of a trough that provides drinking water to livestock. There was no obvious effect on soil Cd concentrations caused by the row of trees forming a shelter belt at the southern end of the paddock.

Within paddock 6, soil Cd concentrations appeared to be inversely related to slope, with the greatest concentrations occurring in the flatter central area of the paddock, and lowest along the western boundary of the paddock where the landform gradually merges into the steeper slopes of paddock 7. In particular, soil Cd concentrations were consistently lower along the northern section of the western fence line of paddock 6, immediately adjacent to the block of native bush that had been fenced off in the toe-slope of paddock 7.

In addition to total Cd concentration, grid soil samples from paddock 18 were also analysed for total P and total C concentration. Correlation analysis (Table 3.5.a) revealed that soil total Cd concentration was positively correlated to both soil total P and total C, although the strength of the correlation was stronger for total P (Spearman's *rho* = 0.709, $P < 0.001$) than total C (Spearman's *rho* = 0.542, $P = 0.004$). Stepwise regression analysis (Table 3.5.b) revealed that soil total C ($P = 0.401$) was not able to improve the prediction of soil total Cd concentration beyond the significant ($P < 0.001$, $R^2 = 0.591$) positive correlation to soil total P.

Table 3.5.a) Spearman coefficient of correlation and significance between soil total Cd and Total P or Total C, and **b)** Stepwise regression analysis for the prediction of soil total Cd concentration based on the independent variables soil total P and total C, for grid soil sampling data ($n = 26$) from paddock 18 of the Waikato farm.

a) Spearman correlation analysis

	Total P	Total C
Correlation coefficient	0.709	0.542
P value	*<0.001*	*0.004*

b) Stepwise regression analysis

Total P	Total C	Regression equation (Total Cd =)	R^2
<0.001	*0.401*	0.00043(Total P) + 0.270	0.591

3.5.1.2 Soil Cd variation with depth

Variation in soil total Cd concentration with soil depth is shown in Figure 3.18 for the eight different sites sampled within the Waikato farm. Consistent with the detailed all-paddock testing data, topsoil (0-150 mm) Cd concentrations descended in the order Kereone > Morrinsville > Topehaehae > Tauwhare.

In all soils, total Cd concentration decreased with increasing soil depth. Soil Cd concentrations were generally greatest in the 0-50 mm depth range (0.40-1.48 mg kg^{-1}) and lowest at 300-350 mm depth (0.03-0.22 mg kg^{-1}). Consistent with the all-paddock testing data that showed little difference in Cd accumulation between effluent and non-effluent paddocks of the same soil type, soil Cd concentration profiles were similar for Kereone soils of equal slope class that had or had not received effluent over the previous 20 years ('4 Ke(A) Eff' and '10 Ke(A)', respectively (Figure 3.18)).

Across the different sampling sites, the total amount of Cd to a depth of 350 mm (corrected for differences in bulk density) ranged between 568-1653 g ha^{-1}, with a mean of 1288 g ha^{-1}. Of this, 51-68% and 75-94% was located in the 0-100 mm and 0-200 mm soil depth ranges, respectively, indicating very little Cd movement below 200 mm depth.

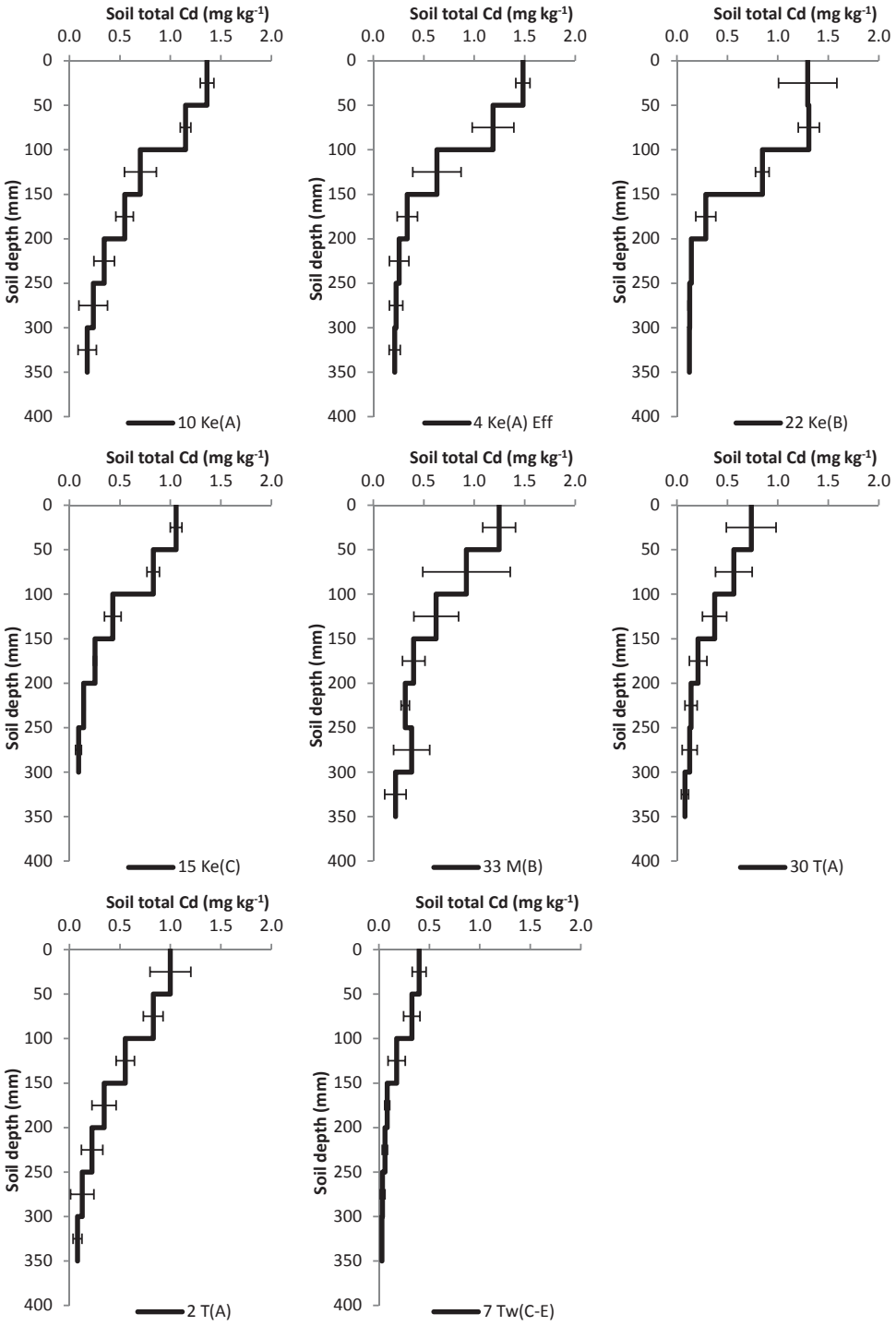

Figure 3.18. Soil Cd concentration with depth for different sites within the Waikato farm (mean of 3 samples, error bars represent standard deviation).

3.5.2 Canterbury farm

3.5.2.1 Spatial variability in soil Cd concentrations

At a sampling depth of 0-75 mm, the mean soil total Cd concentration was 0.36 mg kg^{-1}, with a range of 0.16-0.78 mg kg^{-1} (Figure 3.19). Similar soil Cd concentrations were observed at sampling depths of 75-150 mm (mean 0.31 mg kg^{-1}, range 0.14-0.57 mg kg^{-1}) and 0-150 mm (mean 0.34 mg kg^{-1}, range 0.15-0.64 mg kg^{-1}). The mean soil Cd concentration at the 0-150 mm TFMS 'definitive' sampling depth (FANZ, 2016) therefore represented 94% of that determined at the 0-75 mm standard soil fertility sampling depth, although differences in soil total Cd concentration between different soil depth ranges were not significant overall (*P* = 0.441).

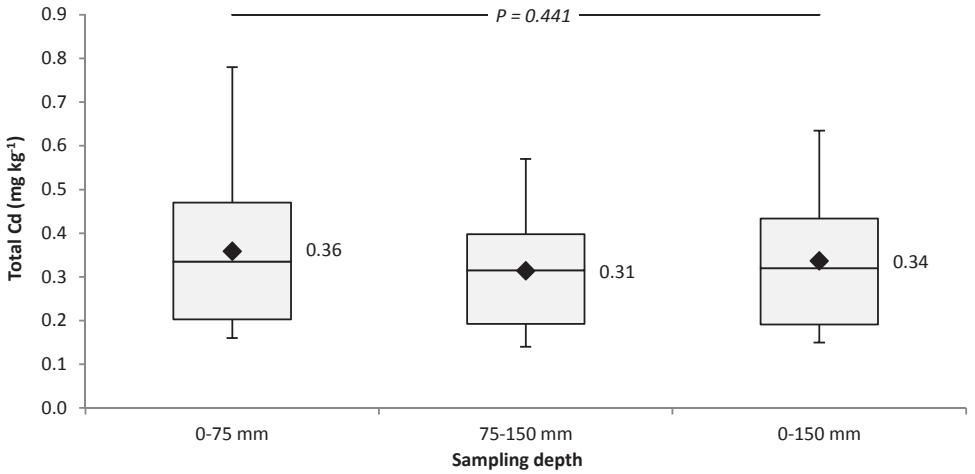

Figure 3.19. Range in soil total Cd concentrations within the Canterbury farm for sampling depths of 0-75, 75-150 and 0-150 mm. Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* value provided for comparison of means.

Soil total Cd was significantly (*P* < 0.001) related to total P, total C, total N, P retention and CEC (Table 3.6), with total P having the strongest correlation (Spearman's *rho* = 0.910). There was also a significant (*P* = 0.004) relationship between Olsen-P and total Cd, however, the strength of this correlation was comparatively weak (Spearman's *rho* = 0.478; Table 3.6). Similar patterns in the paddock-level spatial variability of soil total Cd and total P were evident due to the strong association between these parameters (Figure 3.20 and Figure 3.21).

Table 3.6. Spearman coefficient of correlation and significance between soil total Cd and various soil parameters within the Canterbury farm (0-75 mm sampling depth, *n* = 34).

	Total P	Olsen-P	Total C	Total N	P retention	CEC
Correlation coefficient	0.910	0.478	0.726	0.742	0.622	0.708
P value	*<0.001*	*0.004*	*<0.001*	*<0.001*	*<0.001*	*<0.001*

3.5.2.1.1 Effect of soil type on soil Cd concentration

Soil type had a significant ($P < 0.001$) effect on soil total Cd concentration within the Canterbury farm (Figure 3.22). Without taking into account management block effects, mean soil total Cd concentrations were not significantly ($P > 0.05$) different between the Temuka and Waimairi soil types. However, the Wakanui soil type had a significantly ($P < 0.05$) lower mean soil Cd concentration than both the Temuka and Waimairi soil types.

3.5.2.1.2 Effect of land management history within soil types

Significant ($P < 0.001$) differences in soil total Cd concentrations occurred across the main land management by soil type groupings within the Canterbury farm (Figure 3.23). Within the 'Original dairy' block, soil total Cd concentrations were significantly ($P < 0.05$) greater in the 'Original dairy - Waimairi' group than in the 'Original dairy - Temuka' group, which in turn were significantly ($P < 0.05$) greater than in the 'Original dairy with effluent - Wakanui' group.

Soil Cd concentrations were similar for effluent and non-effluent paddocks within either the Temuka or Wakanui soil types, however comparisons were limited with only one sample for each of the 'Original dairy with effluent - Temuka' and 'Original dairy - Wakanui' groups. Within a soil type, the effect of land management history is evident in the significantly ($P < 0.05$) lower soil Cd concentrations for the 'Ex-cropping/support - Wakanui' group relative to the 'Original dairy with effluent - Wakanui' group. Similarly, the mean Cd concentration of the Waimairi soil type was much greater ($P < 0.05$) for the 'Original dairy' block relative to the 'New undeveloped' block.

Figure 3.20. Inter-paddock soil total Cd (mg kg^{-1}) variability within the Canterbury farm (0-150 mm sampling depth).

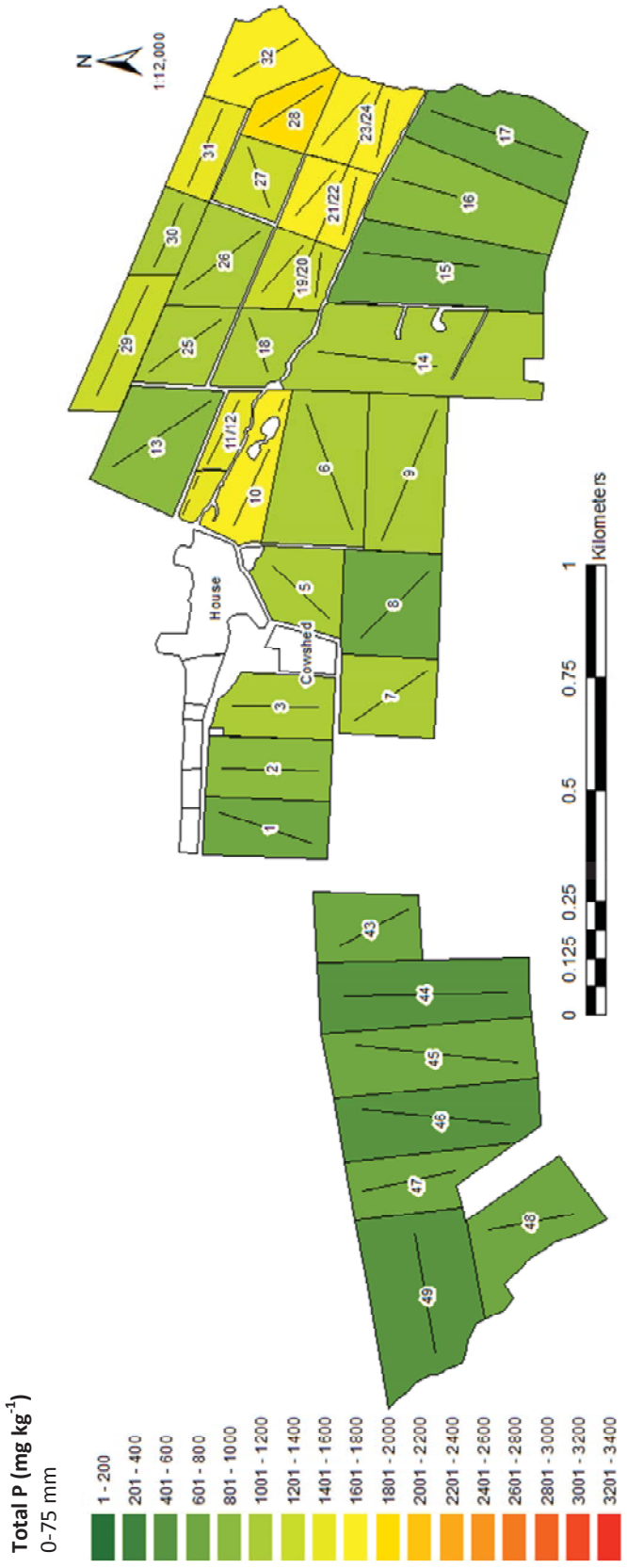

Figure 3.21. Inter-paddock variability for total P (mg kg^{-1}) within the Canterbury farm (0-75 mm sampling depth).

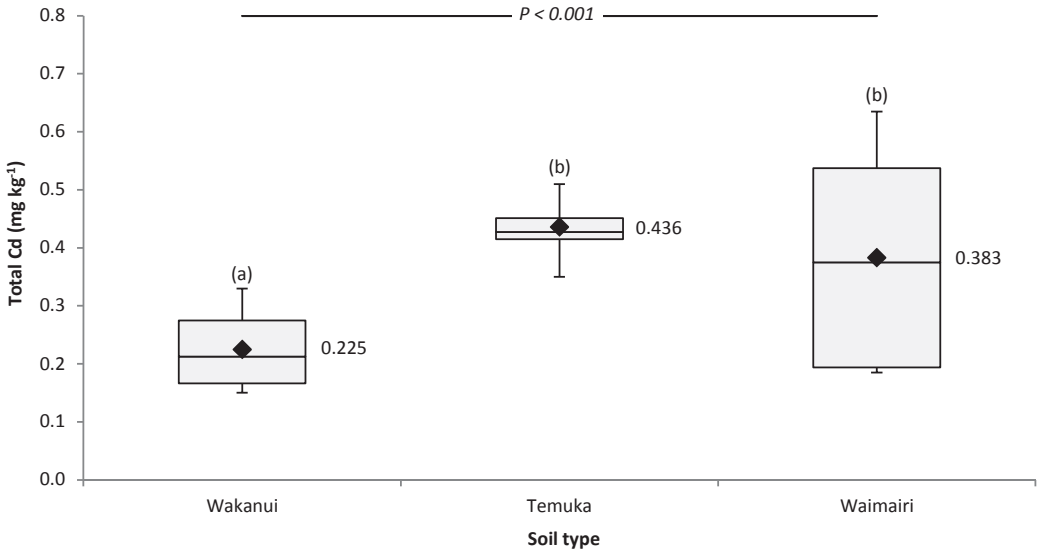

Figure 3.22. Range in soil total Cd concentrations for each soil type within the Canterbury farm (0-150 mm sampling depth). Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* values provided for comparison of means across soil types. Letters in brackets indicate where means are significantly different ($P < 0.05$).

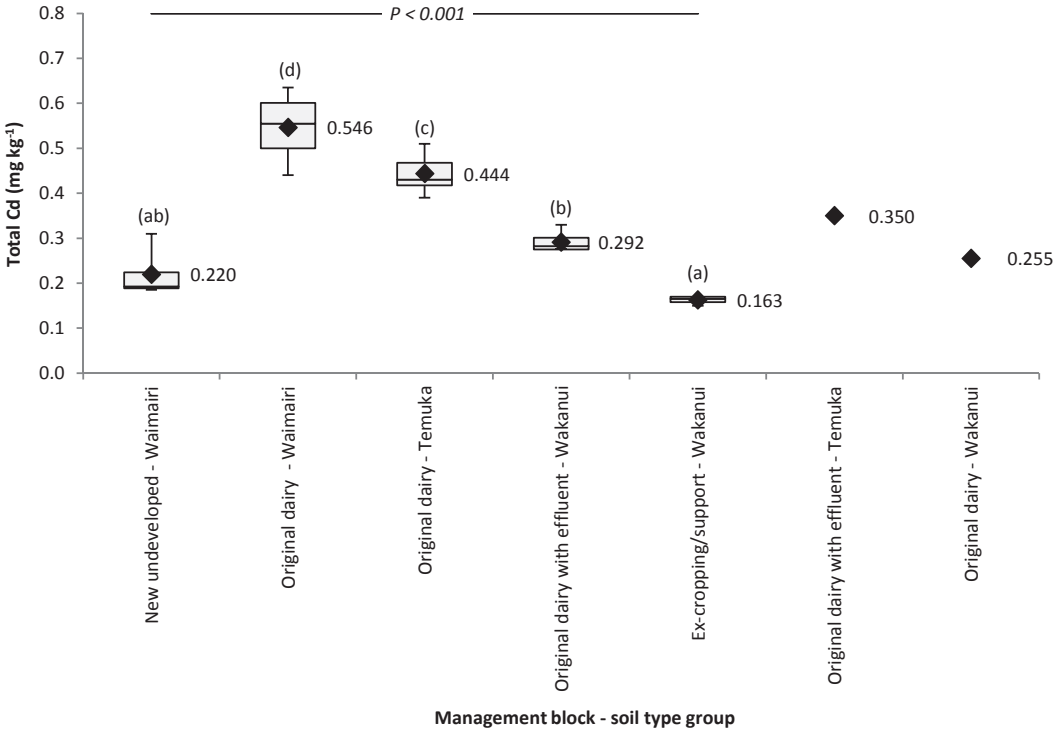

Figure 3.23. Range in soil total Cd concentrations for each land management by soil type grouping within the Canterbury farm (0-150 mm sampling depth). Box and whisker plots represent data quartiles, black diamond and associated value is the mean. ANOVA *P* value provided for comparison of means between groups with more than 1 sample. Letters in brackets indicate where means are significantly different ($P < 0.05$).

The strong positive correlation (R^2 = 0.85, Figure 3.24) between soil total P and total Cd concentration across different land management block and soil type combinations indicates the importance of P fertilisation history on soil Cd accumulation. Exemplifying this, the Waimairi soils within the 'New undeveloped' block have historically received little P fertiliser (as noted by the farm owner), which is reflected in the much lower soil total P levels in that block relative to the Waimairi soils within the 'Original dairy' block. Similarly, the lower soil total P concentrations of the Wakanui soils within the 'Ex-cropping/support' block relative to those within the 'Original dairy' block reflect the lower historic P fertiliser inputs associated with the 'Ex-cropping/support' block.

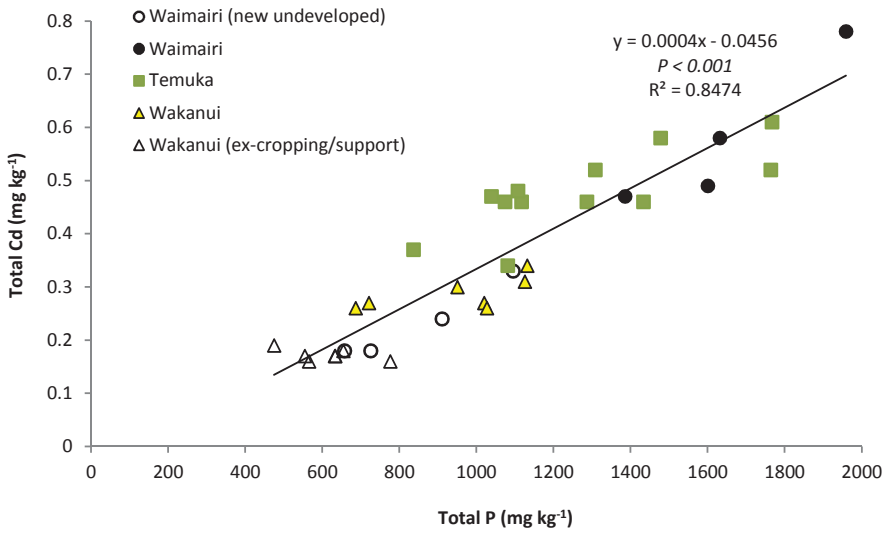

Figure 3.24. Relationship between soil total Cd and total P within the Canterbury farm (0-75 mm sampling depth).

3.5.2.2 Soil Cd variation with depth

Figure 3.25 shows soil total Cd concentration with depth for the ten sites sampled within the Canterbury property. Topsoil (0-150 mm) Cd concentrations within the different sites followed similar trends to the all-paddock testing data, with greatest mean soil Cd concentrations in the Waimairi (28 Wm1) and Temuka (13 Tm2 and 30 Tm1) soils of the 'Original dairy' block (0.54, 0.35 and 0.36 mg kg^{-1}, respectively) and lowest soil Cd concentration for the Wakanui (44 Wk3

and 49 Wk2) and Templeton (45 Te1) soils within the 'Ex-cropping/support block' (0.12, 0.18 and 0.16 mg kg^{-1}, respectively).

The decline in soil Cd concentrations with depth was less exaggerated than in the soils of the Waikato farm, and was not consistent across all sites. For example, sites 1 Wk1, 8 Wk1 and 13 Tm2 (all from the 'Original dairy' block) contained relatively uniform soil Cd concentrations to a depth of approximately 200 mm, before declining thereafter. For site 16 Wm1, soil Cd concentrations over the 0-100 mm depth range were substantially lower than the peak concentrations that were found between 100-250 mm depth, beyond which soil Cd concentrations decreased abruptly. Notably, this paddock had been recently mouldboard ploughed (evident by the gleyed loamy subsoil that had been brought to the soil surface) as part of a pasture improvement program within the 'New undeveloped' block. Similar to the Waikato farm, there was little difference in soil Cd concentrations with depth for cores from the same soil variant representing sites that had or hadn't received dairy shed effluent since 2004 (8 Wk1 and 1 Wk1, respectively; Figure 3.25).

Across the different sites sampled within the Canterbury farm, the total amount of Cd to a depth of 350 mm ranged between 401-877 g Cd ha^{-1}, with a mean of 625 g Cd ha^{-1}. Relative to the Waikato farm, of the total amount of Cd to 350 mm depth, a smaller proportion occurred in the 0-100 mm depth range (27-48%), although similar to the Waikato farm the majority of soil Cd (69-82%) was located within the 0-200 mm soil depth range.

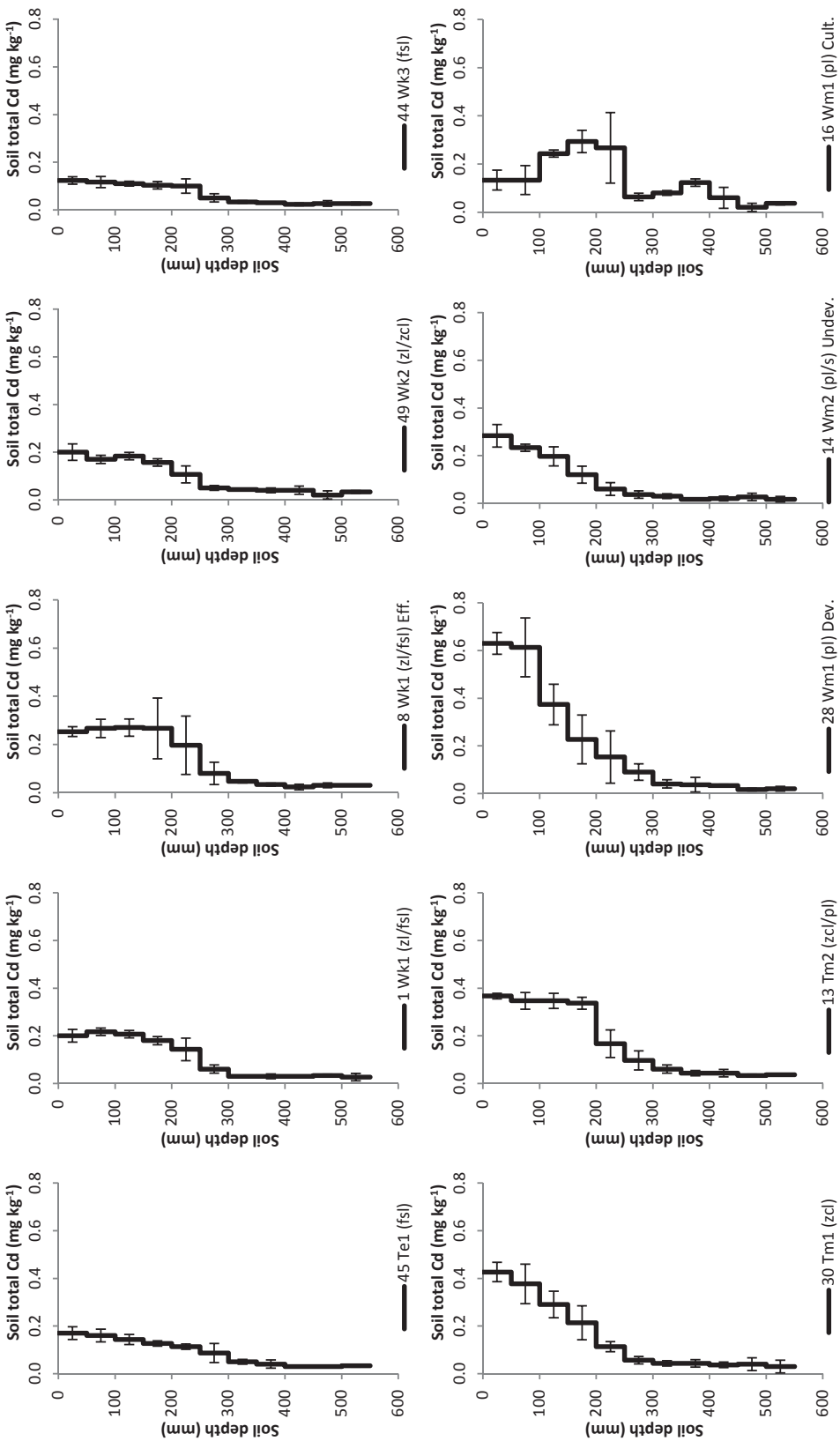

Figure 3.25. Soil Cd concentration with depth for different sites within the Canterbury farm (mean of 3 samples, error bars represent standard deviation).

3.6 Discussion

3.6.1 Factors influencing the spatial variability of soil Cd

3.6.1.1 P fertiliser management

Previous research has shown that soil Cd concentrations in New Zealand agricultural soils are directly correlated to P fertiliser application history (Bramley, 1990; Roberts *et al.*, 1994; Bolan, 1996; Zanders *et al.*, 1999; Loganathan *et al.*, 2003). Consistently, there was a strong correlation (R^2 = 0.84-0.85) between total P and total Cd within both properties of this study (Figure 3.15 and Figure 3.24). The more intensive P fertilisation history of the Waikato property is reflected in its mean 0-150 mm soil total Cd concentration (1.04 mg kg^{-1}) being approximately three times greater than that of the Canterbury property (0.34 mg kg^{-1}). Even when corrected for differences in soil bulk density, the total mass of Cd to 350 mm soil depth in the Waikato property (mean 1288 g ha^{-1}) was approximately double that of the Canterbury property (mean 625 g ha^{-1}).

Although soil organic matter provides an important sorption surface that can influence the retention and mobility of Cd (Gray *et al.*, 1999b, d; Gray *et al.*, 2000) spatial variability in soil total Cd concentration was predicted more strongly by total P concentration than total C concentration, at either the paddock level (Table 3.4 and Table 3.6) or within a paddock (Table 3.5). The tight correlation between total P and total Cd, coupled with the wide range of soil total P concentrations in each property, indicates that P fertiliser management history is the dominant factor influencing variation in soil total Cd concentrations within long-term dairy farms. This is demonstrated by consistently lower total Cd and total P concentrations in blocks that have had less intensive P fertiliser input histories. For example; the 'Nursery' paddock compared to other Kereone soils within the 'Original dairy' block of the Waikato farm (Figure 3.14), and within the Canterbury property, the Waimairi soils in the 'New undeveloped' block

versus those in the 'Original dairy' block, and the Wakanui soils in the 'Ex-cropping/support' block versus those in the 'Original dairy' block (Figure 3.23).

Although both farm owners indicated that uniform P fertiliser application rates have occurred within management blocks, consistent within-paddock variation in P fertiliser inputs over time is likely to explain the intra-paddock variation in soil Cd concentrations seen in paddock 18 and 6 (Figure 3.16 and Figure 3.17, respectively). Normal groundspreader practice is to initially apply fertiliser by driving the outer perimeter of the paddock. As fertiliser application rate typically decreases with increasing distance from the groundspread vehicle (Horrell *et al.*, 1999; Grafton *et al.*, 2013) uniformity in fertiliser application rate is gained by overlap of fertiliser swaths from adjacent application passes. Since there are no adjacent groundspreader passes at the roadside boundary of paddock 18, this application practice will result in lower P fertiliser inputs closer to this boundary fenceline. Further to this, drivers are also likely to have observed a greater driving-line 'setback' along this roadside paddock boundary, so as to avoid direct application of fertiliser onto the public road. These factors are also likely to be partially responsible for the lower soil Cd concentrations detected along the western fence line of paddock 6, adjacent to the area of bush at the eastern toe-slope of paddock 7.

These findings reinforce that soil sampling strategies for assessing soil Cd within long-term dairy farms need to account for variation in P fertilisation history linked to differences in land management. In addition, soil sampling transects need to be placed to avoid zones of non-representative P fertiliser management inputs (e.g. linked to infrastructure or farm layout).

3.6.1.2 Effluent management

Within both properties, there was no consistent difference in soil total Cd concentrations between paddocks of the main dairy platform that had or had not received effluent for 10-20 years. This may be explained by comparative rates of Cd applied in effluent (Table 3.7) and P

fertiliser (Table 3.8) to these blocks. Estimates of Cd applied to the effluent areas of both properties were calculated using the following formula (Equation 1):

$$Cd_{Eff} = (DM_I \times DM_{Cd} \times Exc_{Cd} * Herd * Dung_{DS} * Lact \div Area_{Eff}) \div 1000 \quad (1)$$

Where Cd_{Eff} is the amount of Cd applied annually in effluent (g Cd ha^{-1} y^{-1}), DM_I is the daily dry matter intake (kg DM cow^{-1} d^{-1}), DM_{Cd} is the average Cd concentration in the feed (mg Cd kg^{-1} DM), Exc_{Cd} is the proportion of Cd excreted in dung (%), *Herd* is the average number of cows milked, $Dung_{DS}$ is the proportion of dung excreted in the dairy shed captured (%), *Lact* is the lactation length (days y^{-1}) and $Area_{Eff}$ is the area over which the effluent is spread (ha).

Values for each of the parameters used in Equation 1 are provided in Table 3.7. For $Area_{Eff}$, it is assumed that Cd is primarily associated with the solid component of the effluent, since more than 99% of ingested Cd is excreted in the dung of dairy cattle (Van Bruwaene *et al.*, 1984). Hence, for the Waikato farm where the solids and liquid proportion of effluent are separated and differentially applied, $Area_{Eff}$ applies only to the area receiving effluent solids (paddock 14; 2 ha). In contrast, at the Canterbury farm, effluent is applied as a slurry direct from a sump at the dairy shed, hence the entire effluent area (32 ha) is assumed to receive Cd associated with dung excreted during milking.

Within the Waikato farm, the estimated Cd applied in the effluent-solids to paddock 14 (which does not receive additional P fertiliser) is comparable to that applied in P fertiliser to non-effluent blocks (3.52 and 3.78 g Cd ha^{-1} y^{-1}, respectively). On the basis that paddocks receiving liquid effluent receive little Cd in this effluent, this explains the similar soil Cd concentrations in Kereone soils of effluent solid, effluent liquid and non-effluent paddocks within this property.

Within the Canterbury farm, since land application of effluent began in 2004, effluent paddocks have received approximately half the Cd via P fertiliser and effluent combined (2.85 g Cd ha^{-1} y^{-1}, relative to non-effluent paddocks that received only P fertiliser (6.30 g Cd ha^{-1} y^{-1}). Despite this difference in soil Cd inputs, the limited time period (10 years) over which land

application of effluent and associated differential P fertiliser management has occurred is likely to be the reason behind the lack of any measureable difference in soil Cd concentrations between non-effluent and effluent blocks of this property.

Table 3.7. Estimates of Cd applied in effluent to relevant blocks of the Waikato and Canterbury farms.

	Canterbury	Waikato
DM_I (kg DM cow^{-1} d^{-1})*	16	12
DM_{Cd} (mg Cd $kg\ DM^{-1}$)**	0.13	0.13
Exc_{Cd} (%)***	99%	99%
Herd	500	230
$Dung_{DS}$ (%)****	8%	8%
Lact (days y^{-1})	270	248
$Area_{Eff}$ (ha)	32	2
Cd_{Eff} (g Cd ha^{-1} y^{-1})	0.69	3.52

*Taken from a property-specific OVERSEER 6 nutrient budget

**Ignores feed sources other than pasture. Mean pasture Cd concentration taken from Reiser *et al.* (2014)

***Van Bruwaene *et al.* (1984)

****Ledgard and Brier (2004)

Table 3.8. Estimates of Cd applied in P fertiliser to effluent and non-effluent blocks of the Waikato and Canterbury farms.

Block		Canterbury	Waikato
Non-effluent	Rate of P fertiliser applied (kg P ha^{-1} y^{-1})	35	21
	Amount of Cd applied in P fertiliser (g Cd ha^{-1} y^{-1})*	6.30	3.78
Effluent	Rate of P fertiliser applied (kg P ha^{-1} y^{-1})	12	0
	Amount of Cd applied in P fertiliser (g Cd ha^{-1} y^{-1})*	2.16	0

*Assumes average Cd concentration in P fertiliser of 180 mg Cd $kg\ P^{-1}$ (Rys, 2011)

This analysis suggests that soil Cd is not likely to accumulate at greater rates in effluent blocks relative to non-effluent blocks of dairy farms. In contrast, the total Cd input into effluent paddocks is likely to be less than non-effluent paddocks, since the rate of P fertiliser is reduced (typically by around 50%) in the effluent block of most dairy farms.

3.6.1.3 Soil type

In both properties, a relationship existed between soil total Cd and soil type within common land management units at varying scale (i.e. block and paddock) despite the farm owners of both properties specifically noting that there had been no intentional differentiation in historic P fertiliser inputs to different soils within common land management blocks. This finding contradicts that of Salmanzadeh *et al.* (2016a), who reported that soil Cd concentrations were

not significantly different in three contrasting soils occurring within the same paddock with a common fertiliser history. Despite the uniform-rate approach to P fertiliser inputs within management blocks reported by both farm owners within this study, soil total P concentrations were also significantly ($P < 0.001$) different between soil types within common land management zones in both the Waikato and Canterbury farms (Table 3.9).

Table 3.9. Mean soil total Cd, total P, pH, total C, total N, CEC and P retention for different soil types within common land management units of the Canterbury and Waikato properties.

Farm - block	Soil type	*n*	Total Cd (mg kg^{-1})	Total P (mg kg^{-1})	pH	Total C (%)	Total N (%)	CEC (meq $100g^{-1}$)	P retention (%)
Canterbury - 'Original dairy'	Temuka	12	0.466(b)	1243(a)	6.1	7.0(a)	0.72(a)	33(b)	24(a)
	Wakanui	7	0.287(a)	952(a)	6.1	4.7(a)	0.50(a)	24(a)	16(a)
	Waimairi	4	0.615(c)	1740(b)	6.0	16.2(b)	1.40(b)	61(c)	42(b)
		P value	*<0.001*	*<0.001*	*0.582*	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Waikato - 'New dairy'	Kereone	9	1.356	2594	6.3	8.0	0.81	32	60
	Topehaehae	7	0.820	1489	6.2	5.7	0.54	23	35
		P value	*<0.001*	*<0.001*	0.294	*<0.001*	*<0.001*	*<0.001*	*<0.001*
Waikato - 'Original dairy'	Kereone	15	1.578	2729	6.3	8.6	0.85	33	65
	Topehaehae & Topehaehae+Pakarau	2	1.015	1580	6.3	6.1	0.60	25	39
		P value	*0.011*	*0.008*	*0.711*	*0.020*	*0.015*	*0.015*	*0.009*

3.6.1.4 Slope

An inverse relationship between soil Cd concentration and slope has been previously reported in the literature (Loganathan *et al.*, 1995; Roberts and Longhurst, 2002). This has been attributed to; i) lower grazing residence time on steep slopes and consequent net-export transfer of Cd (deposited in dung) to low slope areas, ii) erosion of Cd-enriched topsoil from steep slopes and transfer to low slope areas, and iii) lower P fertiliser (and consequently Cd) application rate per unit land area in steeply sloping areas.

Although soil Cd concentrations within the different slope classes of the Kereone soil type in the Waikato soil property were not significantly different, there are two possible explanatory factors for this inconsistency with previous research findings. Firstly, the slope classes in the Kereone soil type represented a relatively narrow range of gradients (0-15°). In contrast, the previously reported inverse relationship between slope and soil Cd concentration was

determined from strongly contrasting low, moderate and steeply sloping landform units found in hill country sheep and beef properties (<13°, 13-26° and >26° respectively (Loganathan *et al.*, 1995) and <10°, 10-20° and 30-40°, respectively (Roberts and Longhurst, 2002)). Secondly, most paddocks in the Waikato farm had relatively consistent gradient with only gentle, gradual changes in contour. As a result, incidental variation in the rate of P fertiliser input between slope classes will be minimal, relative to that which is likely to occur in the strongly contrasting slope classes of hill country sheep and beef farms. Furthermore, the relatively consistent, gentle gradient, combined with the high stocking rate and small paddock areas that are typical of dairy systems, will result in more homogeneous dung return and consequently less Cd transfer. In contrast, in the sparsely populated and highly-variable contour of hill country sheep and beef farms, non-uniform dung distribution has been cited as major factor driving slope-related variability in soil accumulation of elements excreted in dung, such as P and Cd (Saggar *et al.*, 1990a; Saggar *et al.*, 1990b; Loganathan *et al.*, 1995; Roberts and Longhurst, 2002).

Exceptions to these general observations are transects 7 , 11 and 13 (Figure 3.10) in the Waikato farm, which had atypically low soil Cd concentrations relative to surrounding paddocks with common management history. In each case these transects represent atypically steep (>15°) landforms. Low soil total P concentrations for the Tauwhare hill soil (Transect 7; Figure 3.11) and for transects 11 and 13 relative to the majority of Kereone soils (Figure 3.15) indicates that lower P fertiliser inputs per unit land area could be responsible for the low soil total Cd concentrations. In addition, it is possible that greater topsoil erosion in these steep zones could be a factor, given that Cd and P are both relatively immobile and tend to accumulate near the soil surface (Loganathan and Hedley, 1997) making soil Cd and P more susceptible to soil particulate movement. Finally, consistent with the animal transfer hypothesis used to explain soil P and Cd variability in hill country pastures (Saggar *et al.*, 1990a; Saggar *et al.*, 1990b; Loganathan *et al.*, 1995; Roberts and Longhurst, 2002) non-uniform dung

returns driven by variation in grazing residence time could also contribute to the low soil P and Cd concentrations in the atypically steep areas represented by transects 7, 11 and 13. Overall, the results from these three atypically-steep transects in comparison to the other transects indicates that the distribution of soil Cd in intensively grazed, well subdivided dairy systems is only likely to be influenced when slope exceeds 15°.

3.6.2 Variation in soil Cd distribution with depth

The decrease in soil Cd concentrations with increasing soil depth as seen in both properties of this study is consistent with the available literature relevant to grazed pastoral systems (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999). Because of this non-uniform depth distribution of soil Cd, depth of soil sampling influences the Cd concentration determined for a land unit. The all-paddock testing data from this study revealed that the mean soil Cd concentration at a sampling depth of 0-150 mm represented 94% and 82% of that assessed at 0-75 mm for the Canterbury and Waikato farms, respectively. These proportions are greater than those reported previously for fertilised pastoral farms (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Zanders *et al.*, 1999) with the exception of the 'low P fertiliser' pastures assessed by Loganathan *et al.* (1995) (Table 3.10).

Table 3.10. Comparison of soil total Cd concentrations assessed at 0-150 mm and 0-75 mm by various authors in New Zealand grazed pastoral systems.

Author	Soil	Total Cd (mg kg^{-1})		Total Cd conc. at 0-150 mm relative to 0-75 mm (%)
		0-150 mm	0-75 mm	
Roberts *et al.* (1994)	Allophanic (YBL)	0.47	0.67	70%
	Pumice (YBP)	0.27	0.35	79%
Zanders *et al.* (1999)	Allophanic	0.36	0.53	68%
	Ultic	0.28	0.46	61%
Loganathan *et al.* (1995)	High P fertiliser - Low slope	0.27	0.41	67%
	High P fertiliser - Med slope	0.18	0.25	70%
	High P fertiliser - Steep slope	0.15	0.22	68%
	Low P fertiliser - Low slope	0.10	0.11	86%
	Low P fertiliser - Med slope	0.07	0.08	88%
	Low P fertiliser - Steep slope	0.05	0.06	84%

As supported by the data of Cavanagh (2014b), greater divergence in soil Cd concentrations measured at 0-150 mm and 0-75 mm might be expected as soil Cd concentration increases,

due to the limited mobility of Cd in the soil and greater accumulation near the soil surface. This is consistent with the wider ratio of soil Cd at 0-75 mm and 0-150 mm for the 'high P fertiliser' pastures relative to the 'low P fertiliser' pastures of Loganathan *et al.* (1995), as well as the higher-Cd Waikato soils relative to the lower-Cd Canterbury soils in this study.

As ploughing and cultivation is known to redistribute and homogenise Cd within the soil profile (Roberts *et al.*, 1995; Chen *et al.*, 2009) the narrower ratio of soil Cd measured at 0-150 mm and 0-75 mm depths for the Canterbury property relative to the Waikato property is also likely to reflect the different soil tillage histories of the two properties. Whereas the Waikato property has been managed under a no-tillage philosophy, the Canterbury property has a strong history of soil tillage through regular cropping and pasture renewal. The effect of recent mouldboard ploughing is clearly seen in the 'inverted' soil Cd concentrations within the 0-200 mm depth range for site 16 Wm1 (Figure 3.25). Soil tillage is also likely to explain the relatively uniform soil Cd concentrations in the 0-200 mm depth range for soil profiles 1 Wk1, 8 Wk1 and 13 Tm2 (Figure 3.25) with all of these paddocks having gone through pasture renewal processes within the last 10-20 years.

Although the TFMS caters for the standard soil fertility sampling depth of 0-75 mm to be used for property screening purposes, the variation in soil Cd with depth (linked to soil type, P fertiliser management and tillage history) supports the use of the FANZ-recommended 0-150 mm definitive sampling depth to standardise soil Cd assessment between properties.

3.6.3 Influence of sampling strategy on soil Cd assessment

Under the TFMS, farms are classed within five different soil Cd management tiers, based on their property-mean soil total Cd concentration (Cavanagh, 2012). However, several options exist to quantify a property-mean soil total Cd concentration. Table 3.11 compares three different approaches for the determination of a property-mean soil Cd concentration for each of the Waikato and Canterbury farms. These were; i) a simple mean, calculated across all

available all-paddock testing sample results, ii) a weighted mean, calculated as the sum of each soil Cd concentration weighted by the proportion of the total effective farm area that they represent, and iii) the FANZ-recommended definitive sampling approach for LMU Cd assessment (summarised in Table 3.1), with LMU means weighted by proportion of the property effective area.

Table 3.11. Comparison of property-mean soil Cd concentrations determined using different assessment criteria, for the Waikato and Canterbury farms.

Sampling methodology	Property-mean Cd concentration (mg kg^{-1})	
	Waikato	Canterbury
Mean of all APT samples	1.04	0.30
All APT samples weighted by representative area	1.07	0.34
FANZ protocol with 6 monitor paddocks per main LMU (potential range)	1.03 - 1.18	0.29 - 0.30

Following the FANZ-recommended soil sampling protocols, the Waikato farm was subdivided into four main land management units; 1) Original dairy - Kereone, 2) Original dairy with effluent - Kereone, 3) New dairy - Kereone, and 4) Topehaehae. Within this assessment, transects 7, 11 and 13 were considered non-representative of their respective management blocks due to atypical slope/contour, and as such were not included as 'potential' monitor paddocks. The 'Nursery' paddock (transect 20) was also excluded as a non-representative paddock based on its unique management history and small size. Transects 2 (Topehaehae+Pakarau) and 33 (Morrinsville) represent unique soil types within the property, but being similar in composition and management history to surrounding Topehaehae and Kereone soils, respectively, these paddocks were tied to the LMU groups representing the latter soils. Similarly, transect 17F (representing a small area of Topehaehae soil within the 'Original dairy' block) was linked to a larger group of Topehaehae soil samples from the 'New dairy' block.

Application of the FANZ protocol to the Canterbury property resulted in five main LMUs being identified; 1) Original dairy - Temuka, 2) Original dairy - Waimairi, 3) Original dairy with recent effluent - Wakanui, 4) Ex-cropping/support - Wakanui, and 5) New undeveloped - Waimairi.

Although the FANZ protocol stipulates a minimum of six monitor paddocks per LMU and that LMUs with small numbers of paddock be avoided, the isolation of the 'New undeveloped - Waimairi' LMU (four paddocks) was justified due to its unique management history and large area (approximately 20% of the total farm area). In-line with the FANZ protocol, one paddock representing a Wakanui soil within the original dairy farm that had not received effluent (transect 1) was tied to the 'Original dairy with recent effluent - Wakanui' LMU, as the best fit. Similarly, two transects (45 and 22/23) that represented small areas of mixed soils (Templeton + Wakanui and Waimairi + Temuka, respectively; Figure 3.5) were tied to larger LMUs ('Ex-cropping/support - Wakanui' and 'Original dairy - Waimairi', respectively).

Based on the minimum of six monitor paddocks per LMU (with the exception of the 'New undeveloped - Waimairi' LMU) the potential weighted-mean soil Cd concentration (i.e. corrected for the proportion of each LMU of the total farm area) for the Waikato and Canterbury properties could range between 1.03-1.18 and 0.29-0.30 mg kg^{-1}, respectively (Table 3.11) depending on which specific paddocks are sampled. The greater range in soil Cd concentrations for the Waikato property reflects the greater variation in soil Cd concentrations within that property. Therefore, while the FANZ-recommended sampling protocol minimises the amount of soil sampling required, there will be greater risk of deviation from the true mean soil Cd concentration for the LMU or property overall.

However, the FANZ-recommended sampling protocol also recommends sampling every paddock when a TFMS soil Cd trigger value for tier 2, 3 or 4 (1.0, 1.4 or 1.8 mg kg^{-1}, respectively) is being approached. The rationale behind this is that under the TFMS, increasing restrictions to P fertiliser management apply with increasing soil Cd concentration (FANZ, 2016), thus placing greater emphasis on ensuring soil Cd assessment is as accurate as possible. Sampling every paddock, ensuring that the different soils within each LMU are represented, and then weighting these results based on their respective proportions of the total effective farm area, will provide a more robust assessment of the property-mean soil Cd concentration

(1.07 and 0.34 mg kg^{-1} for the Waikato and Canterbury properties, respectively; Table 3.11) than simply averaging the results of all samples (1.04 and 0.30 mg kg^{-1} for the Waikato and Canterbury farms, respectively; Table 3.11). Where definitive and accurate assessment of a property's mean soil Cd concentration is desired, it is therefore recommended that all paddocks should be sampled individually, with individual results weighted on their respective proportion of the total effective farm area, and then summed to provide a property weighted-mean soil Cd concentration.

3.6.4 Identification of soils and sites for future trial work

Soils within the Waikato farm formed the basis of subsequent pot- and field-based agronomic research. Within this property, the relationship between soil total Cd concentration and soil type within zones of common P fertiliser management provides an excellent basis for identifying soils and sites suitable for future pot and field trials. Furthermore, the intra-paddock soil Cd variability assessment that was carried out in two paddocks (18 and 6) provides useful insight into paddock features (e.g. terrain and infrastructure/layout) that can induce unnecessary and avoidable variability in soil Cd concentrations.

Within the Waikato farm, the predominant Kereone and Topehaehae soils (Allophanic and Gley soil orders, respectively) provide suitably contrasting soils from which to evaluate factors influencing soil Cd phytoavailability and plant Cd accumulation. In addition to differences in their soil total Cd concentration, these soils also contrast each other in terms of organic matter content and clay mineralogy (inferred by differences in P retention and CEC; Table 3.9); key factors known to influence soil Cd phytoavailability (McBride, 1989; Backes *et al.*, 1995; McBride *et al.*, 1997; Naidu *et al.*, 1997; Gray *et al.*, 1999d; Loganathan *et al.*, 2012).

Based on the detailed soil survey and soil analysis carried out within the Waikato farm, suitable sites representing Kereone and Topehaehae soil types were located in paddocks 2 and 29, respectively (Figure 3.3). Soil was sourced from these locations for a pot trial investigating the

effects of soil moisture on Cd phytoavailability (Chapter 7). Originally, it was intended that these sites would also be used for the location of field trials investigating the effect of soil pH modification on plant Cd accumulation (Chapter 8). However, after subsequent discussion with the farm owner, for practical reasons it was decided to shift the Topehaehae field trial site to paddock 1 (Topehaehae soil; Figure 3.3) so as to improve access to the site while minimising disturbance to livestock and day-to-day farm management.

Although soils from the Canterbury farm were not used for further pot- or field-based agronomic research within this thesis, the detailed soil Cd data and soil maps that were generated for this property provide excellent baseline knowledge, from which to leverage future research (e.g. to study the effects of cultivation and other mitigation strategies on soil Cd phytoavailability).

3.7 Conclusions

This research shows large differences in the mean soil Cd concentrations of two long-term dairy farms, with these differences primarily driven by differences in P fertilisation history. However, within both properties there was also wide variation in soil Cd concentrations, with variation in historic P fertiliser management practices and soil type being the primary drivers of soil Cd spatial variation. Slope class (only a factor in the Waikato farm) only exerted an influence on soil total Cd concentrations when slope exceeded 15°. No clear trends in soil Cd concentration could be determined between effluent and non-effluent paddocks of either property. Calculations of Cd applied to soils in dairy shed effluent support this finding; where farmers decrease P fertiliser application rates in recognition of the P applied within the recycled effluent, total Cd inputs in effluent blocks are likely to be similar to or less than in blocks receiving P fertiliser alone.

Within common land management by soil type groupings, there was still considerable inter-paddock (and intra-paddock) variation in soil Cd concentrations. Under the TFMS, where soil

Cd is enriched and greater restrictions to P fertiliser management options apply, it is recommended that all paddocks are tested independently, with individual results weighted (based on representative area as a proportion of the total farm area) and summed to provide the most robust assessment of the property mean soil Cd concentration. Given the variability between paddocks of common soil type and management history, this approach will also assist decision making with regard to land management suitability for specific land units (e.g. locations for planting specialist forage crops to minimise livestock dietary Cd exposure). Finally, variation in the ratio of soil total Cd assessed at 0-75 and 0-150 mm depth supports use of a 0-150 mm 'definitive' sampling depth (FANZ, 2016) to provide consistency between properties with differing land use, soil tillage and P fertiliser management history, and soil type.

CHAPTER 4 : Cadmium accumulation by different forage species used in New Zealand livestock grazing systems

This chapter was published in *Geoderma Regional* in 2016. Citation:

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.

4.1 Abstract

Cadmium (Cd) accumulation in 12 forage plant species was investigated in a glasshouse trial. Potted soil (total Cd 0.43 mg kg^{-1}) was fertilised with varying rates of superphosphate to manipulate phosphorus availability, plant growth rate and soil Cd availability. Mean tissue Cd concentration decreased in the order chicory > plantain > turnip > lucerne > sheep's burnet > strawberry clover > kale > perennial ryegrass > haresfoot trefoil > red clover > crimson clover > white clover. Chicory and plantain had significantly greater mean tissue Cd concentrations (1.639 and 0.734 mg kg^{-1} DM, respectively) than all other species. Rate of superphosphate and plant yield had little influence on plant tissue Cd concentration. The correlation between soil total Cd and plant tissue Cd concentration was generally poor (R^2 = 0.006-0.428) and was only significant for perennial ryegrass and red clover. Modelling of lamb kidney Cd accumulation indicated that food standard maximum levels may be exceeded in animals younger than the current meat industry 30 month offal discard age. With increased use of chicory and plantain as specialist forage crops in New Zealand, this information will be important for improving livestock Cd accumulation risk assessment models.

4.2 Introduction

New Zealand is heavily dependent on revenue generated from ruminant grazing systems, with dairy, meat and edible offal accounting for approximately 40% of total export earnings

(Treasury, 2016). To sustain intensive pasture production from New Zealand's naturally low phosphorus (P) status soils regular P fertiliser application is necessary (McLaren and Cameron, 1996). Historically phosphate rocks used for local superphosphate manufacture were rich in Cd (Loganathan *et al.*, 2003). Cd accumulation in New Zealand agricultural soils is strongly correlated to P fertiliser application history (Bramley, 1990; Roberts *et al.*, 1994).

Although the native Cd concentrations in New Zealand agricultural soils are similar to concentrations found worldwide (Roberts *et al.*, 1994; McDowell *et al.*, 2013) ongoing soil Cd accumulation is undesirable. This is because plants have little ability to regulate Cd uptake; and, as a consequence, plant tissue Cd concentration increases with increasing soil Cd concentration (Adriano, 1986; Smolders and Mertens, 2012). Left unmanaged, Cd accumulation in agricultural soils has potential to increase Cd concentration in food products, thereby increasing human dietary Cd intake.

In 2011, a Tiered Fertiliser Management System (TFMS) was introduced to manage on-going soil Cd accumulation in New Zealand agricultural land (MAF, 2011). Within the TFMS, five soil Cd management tiers are defined based on four soil total Cd trigger concentrations; 0.6, 1.0, 1.4 and 1.8 mg kg^{-1} soil dry weight (Cavanagh, 2012). The basic premise of the TFMS is that as soil Cd tier-status increases, increasing restrictions apply to P fertiliser type and/or rate of application, so as to manage further Cd inputs and minimise on-going soil Cd accumulation. Beyond the uppermost trigger value of 1.8 mg kg^{-1}, no further soil Cd accumulation is permitted, without a site-specific risk investigation being undertaken (Warne, 2011). Although the TFMS provides a suitable basis for managing soil Cd accumulation, it is not designed to specifically manage risks arising from plant Cd accumulation in agricultural systems. This is because soil Cd phytoavailability is influenced by a range of soil factors (McBride *et al.*, 1997; Gray *et al.*, 1999d, c; Li *et al.*, 2003), and because plant Cd accumulation is both species and cultivar specific (Florijn and Van Beusichem, 1993; Gray *et al.*, 1999a; Gray *et al.*, 2001; Gray and McLaren, 2005; Smolders and Mertens, 2012).

Ruminant-grazed pastoral systems represent the predominant agricultural land use in New Zealand, accounting for approximately 12 million hectares (StatsNZ, 2013). Although more than 99% of dietary Cd is excreted (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) Cd is known to accumulate in the liver and kidney of livestock due to high levels of metallothionein synthesis in these tissues (Lee *et al.*, 1994; Lee *et al.*, 1996). Because of the efficiency of these organs at sorbing and storing metals, Cd is not expressed in significant quantities in either meat or milk products (Solly *et al.*, 1981; Sharma *et al.*, 1982; Morrison, 1988).

To minimise the risk of food standard Cd maximum level (ML) exceedances in livestock liver and kidney tissue, the New Zealand meat industry currently discards ruminant liver and kidney from trade for human consumption for animals older than 30 months (MAF, 2008). However, exceedances in animals younger than 30 months were first predicted by the modelling of Loganathan *et al.* (1999), with increased liver and kidney Cd accumulation being linked to increased dietary Cd exposure (Lee *et al.*, 1994; Lee *et al.*, 1996).

Soil ingestion (estimated for sheep at 0.06-0.1 kg day^{-1} (Healy, 1967; Rodrigues *et al.*, 2012) and dairy cows at 0.25-1.24 kg day^{-1} (Healy, 1968; Rodrigues *et al.*, 2012)) can contribute to total livestock dietary Cd intake, however the majority (approximately 90%) occurs via the forage they consume (Lee *et al.*, 1996; Roberts and Longhurst, 2002). Because of this, grazing stock on Cd-rich forages may result in more rapid kidney/liver Cd accumulation, potentially leading to more frequent exceedance of food standard MLs.

While substantial research into plant Cd accumulation was undertaken during the 1990's, the majority of historic research on animal forages has been focussed on ryegrass and clover species (literature review, Table 2.10). The common theme of literature is that Cd concentrations in ryegrass-white clover pastures are relatively low, with concentrations typically being greater for ryegrass than white clover (Roberts *et al.*, 1994; Loganathan *et al.*,

1997; Gray *et al.*, 1999a, c). Roberts *et al.* (1994) reported that the Cd concentration in unspecified pasture weed species was significantly greater than both grass and clover species. Parker *et al.* (2008) reported Cd concentrations of a plantain/chicory/red clover/white clover forage stand to be approximately 4-5 times greater than an adjacent ryegrass-white clover pasture, however species-specific data was again not presented and soil Cd data was not included.

Since the 1990's, there has been significant diversification in New Zealand farms systems with the integration of a variety of new forage species for which there is little documented information on Cd uptake and accumulation. For example, summer- and winter-grazed forage brassicas are integral in providing a reserve of high quality feed for livestock when pasture growth rate and/or quality is poor. Furthermore, chicory and plantain are increasingly being sown as monoculture stands or in combination with red or white clover, due to their high feed quality, growth rate and persistence over the hot, dry summer period, which traditional ryegrass-white clover pastures struggle to tolerate. Developing Cd accumulation data for key forage species used in modern farm systems is therefore desirable to improve sensitivity and accuracy of animal Cd accumulation models (Reiser *et al.*, 2014) and to ensure that appropriate Cd management strategies are developed and implemented on-farm. The study described in this paper was carried out with the purpose of initiating this data collection.

4.3 Methodology

A glasshouse pot trial was designed to test the relative potential for twelve forage species to take up and accumulate P and Cd in their above ground vegetative tissue (data on P uptake and accumulation are presented in McDowell and Cosgrove (2015)). Soil was collected from the A horizon (10-15 cm depth) of a commercial dairy farm in the district of Hillend, near Balclutha in South Otago (Table 4.1). After collection, the soil was air dried and sieved (<2 mm) before being transferred into pots.

Table 4.1. Description and characteristics of soil used in the trial.

Soil type:		Waitahuna deep silt loam, rolling phase			
New Zealand Soil Classification (NZSC):		Mottled Fragic Pallic soil			
USDA Taxonomy:		Typic Hapludalfs			
Organic matter (%)	Total C (%)	Total P (mg kg^{-1})	Total Cd (mg kg^{-1})	pH	Olsen-P (mg L^{-1})
6.3	3.6	775	0.43	5.6	10

Two different pot sizes were used in this trial. 15 cm diameter pots containing 2.5 kg of air-dried soil were used for ryegrass, legume and herbaceous species and an unplanted 'fallow' treatment (plant species 1-10; Table 4.2). Larger pots (22 cm diameter) containing 4 kg of air-dried soil were used for the two brassica species (plant species 11 & 12; Table 4.2).

Table 4.2. Plant species assessed in the trial.

Species		Cultivar	Approximate seed sowing rate (kg ha^{-1})
1	Perennial ryegrass (*Lolium perenne*)	Trojan	22
2	White clover (*Trifolium repens*)	Huia	8
3	Red clover (*Trifolium pratense*)	Hamua	15
4	Lucerne (*Medicago sativa*)	Wairau	15
5	Crimson clover (*Trifolium incarnatum*)	Blaza	15
6	Strawberry clover (*Trifolium fragiferum*)	Palestine	10
7	Haresfoot trefoil (*Trifolium arvense*)	Increase	6
8	Sheep's burnet (*Sanguisorba minor*)	-	10
9	Chicory (*Cichorium intybus*)	Puna II	5
10	Plantain (*Plantago lanceolata*)	Tonic	4
11	Kale (*Brassica oleracea*)	Gruner	4
12	Turnip (*Brassica rapa*)	Barkant	2

Lime (laboratory grade $CaCO_3$) was mixed into each pot at 1400 mg kg^{-1} (approximately equivalent to 2000 kg ha^{-1}) with the purpose of increasing soil pH to within the agronomic optimum range of 5.8-6.0. Calcium sulphate and potassium chloride were mixed into the soil (both at 500 mg kg^{-1}) prior to planting.

4.3.1 P fertiliser treatments

To modify soil P and Cd availability, superphosphate (9.5% Total-P, 9.0% P soluble in 2% citric acid, and 168 mg Cd kg^{-1} P) was ground and mixed into the potted soil. In addition to a control (zero P fertiliser), plant species 1-10 and an unplanted fallow treatment received superphosphate at 200, 400, 600, 800 and 1000 mg kg^{-1} soil (equivalent to 19, 38, 57, 76 and 95 mg P kg^{-1} soil, and 0.0032, 0.0064, 0.0096, 0.0128 and 0.0160 mg Cd kg^{-1} soil, respectively)

while plant species 11 & 12 were limited to two superphosphate rates; 600 and 1400 mg kg^{-1} soil (equivalent to 57 and 133 mg P kg^{-1} soil, and 0.0096 and 0.0233 mg Cd kg^{-1} soil, respectively). Following fertiliser mixing, the soil was watered to near field capacity using deionised water and then allowed to dry over a 15 day period. This process was repeated for two further cycles, allowing the fertilised soil to equilibrate.

Seeds of each plant species were sown into pots at the rates designated in Table 4.2 on 12 March 2013 (day 0). Plant species 1-10 and the unplanted fallow soil had four replicates at each of the six soil fertility levels (264 pots). Plant species 11 and 12 had three replicates at each of the three soil fertility levels (18 pots). Following sowing, all 282 pots were laid out in the glasshouse in a randomised design. During the trial period, an unidentified soil borne disease resulted in a number of plant failures. This reduced the total number of 'viable' replicates sampled for the trial (details for total soil and plant species replicates sampled are provided in Table 4.3).

4.3.2 Trial management and analyses

Temperature within the glasshouse was regulated to prevent heat or cold stress affecting growth, with a mean temperature of 15 °C (range 12-27 °C) over the term of the trial. All pots were hand-irrigated with deionised water every second day so as to maintain soil moisture between field capacity and wilting point, with minimal induced drainage. All pots received additional potassium chloride and calcium sulphate (each at 500 mg kg^{-1}), split between two applications on day 205 and 207. Pots containing perennial ryegrass and herb species (species 1 & 8-10 in Table 4.2) received ammonium nitrate fertiliser at 50 mg kg^{-1} (approximately 25 kg N ha^{-1} equivalent) on day 241 to alleviate nitrogen deficiency that was apparent in these species after multiple harvests.

The two brassica species were harvested once only, 270 days after planting. Multiple harvests occurred for all other species, with these occurring on day 73, 108, 143, 177, 217 and 266. The

vegetative tissue of kale and turnip was separated into leaf and storage organ components. No separation of vegetative tissue occurred for other plant species. The bulb of the turnip plants was thoroughly washed to remove any soil before it was dried and ground for analysis. Above-ground foliage from other plant species was harvested 2 cm above the soil surface and was not washed since it was not in direct contact with the soil. Biomass collected from each individual replicate at each harvest was oven-dried at 65°C for 24 hours to determine dry matter (DM) yield. Tissue subsamples from each harvest were retained and aggregated for each replicate for total Cd analysis.

Following the final harvest, soil samples (0-75 mm) were taken from each pot, air-dried and passed through a 2 mm sieve. These were then analysed for plant available phosphorus (Olsen-P; as outlined in Blakemore *et al.* (1987)) and total Cd using Inductively Coupled Plasma Optical Emission Spectroscopy after digestion with nitric acid and hydrogen peroxide (Kovács *et al.*, 2000). The detection limit for total Cd analysis was 0.00026 mg kg^{-1} DM. Reference soil (Wageningen ISE 981, ISE 921) and plant (Wageningen IPE 100, IPE 151) standards and blanks (acid-only) were included within digestion runs of 40 samples. Reference standards were measured at the beginning and end of each analysis run, and calibration rescale was performed every 20 samples.

Statistical analysis was carried out using the software SPSS (IBM Corp, 2013). Analysis of variance (ANOVA) was undertaken to assess whether treatment means were different due to variation imposed by different factors (e.g. rate of superphosphate and forage species). Tukeys honestly significant difference (HSD) was run as a post-hoc analysis to identify individual treatment means that were different. Linear regression analysis was performed on plant tissue Cd concentration and soil total Cd, and plant tissue Cd concentration and plant yield. The discussion of results is limited to those that met the threshold for significance of comparative tests and regression of $P < 0.05$.

4.4 Results and discussion

4.4.1 Soil total Cd and Olsen-P

Table 4.3 presents mean soil Olsen-P (mg L^{-1}) and total Cd (mg kg^{-1}) concentration for each superphosphate application rate. Olsen-P levels were influenced by the rate of superphosphate application (Table 4.3), ranging between 10.6 mg L^{-1} (control) and 44.8 mg L^{-1} (superphosphate at 1400 mg kg^{-1}).

Increasing the rate of superphosphate application increased the soil total Cd concentration (Table 4.3). Mean soil total Cd levels as a function of superphosphate treatment varied between 0.445 mg kg^{-1} (superphosphate at 200 mg kg^{-1}) and 0.582 mg kg^{-1} (superphosphate at 1400 mg kg^{-1}).

4.4.2 Plant yield

Differences were apparent in the mean yield (kg DM ha^{-1}) of the 12 plant species (Table 4.3). Overall, mean species yield (kg DM ha^{-1}) decreased in the order red clover > kale leaf > turnip bulb > haresfoot trefoil > turnip leaf > white clover > plantain > kale stem > perennial ryegrass > crimson clover > strawberry clover > sheep's burnet > chicory > lucerne (Table 4.3).

A dry matter yield response to increasing rate of superphosphate only occurred for haresfoot trefoil (Table 4.3). Although yield increases with increasing rate of superphosphate were not significant for other species, there was a general trend for increased dry matter yield with increasing rate of superphosphate application. In particular, this was the case for members of the *Trifolium* and *Brassica* genera that are known to be P responsive at low fertility (Morton *et al.*, 1998a; Wilson *et al.*, 2006; Maxwell *et al.*, 2013).

Table 4.3. Effect of rate of superphosphate on soil Olsen-P (mg L^{-1}) and total Cd (mg kg^{-1}), and plant yield (kg DM ha^{-1}) and tissue Cd concentration (mg kg^{-1} DM) for individual plant species. Mean yield (kg DM ha^{-1}) and tissue Cd concentration (mg kg^{-1} DM) are also presented by plant species. Numbers followed by the same letter are not significantly different from one another ($P < 0.05$).

Plant species	Parameter	*n*	Superphosphate added (mg kg^{-1}) 0	200	400	600	800	1000	1400	*P* value	Mean yield* (kg DM ha^{-1})	Mean tissue Cd* (mg kg^{-1} DM)
All	Olsen-P (mg L^{-1})**	257	10.6(a)	12.9(ab)	18.4(bc)	21.7(cd)	25.3(de)	30.5(e)	44.8(f)	*<0.001*		
	Total Cd (mg kg^{-1})**		0.446(a)	0.445(a)	0.458(a)	0.458(a)	0.469(a)	0.464(a)	0.582(b)	*<0.001*		
Perennial ryegrass	Plant yield (kg DM ha^{-1})	22	2135	2114	2174	1932	2196	1899		*0.888*	2075(ab)	
(*Lolium perenne*)	Tissue Cd (mg kg^{-1} DM)		0.088	0.105	0.108	0.101	0.099	0.119		*0.201*		0.103(abc)
White clover	Plant yield (kg DM ha^{-1})	22	1898	2131	2220	2304	2970	2697		*0.708*	2370(bc)	
(*Trifolium repens*)	Tissue Cd (mg kg^{-1} DM)		0.040	0.034	0.027	0.036	0.020	0.055		*0.637*		0.035(a)
Red clover	Plant yield (kg DM ha^{-1})	21	4313	7058	6437	6386	6253	8048		*0.069*	6416(f)	
(*Trifolium pratense*)	Tissue Cd (mg kg^{-1} DM)		0.051	0.044	0.057	0.073	0.056	0.073		*0.377*		0.059(ab)
Lucerne	Plant yield (kg DM ha^{-1})	23	1400	1242	1401	1538	1548	1457		*0.756*	1431(a)	
(*Medicago sativa*)	Tissue Cd (mg kg^{-1} DM)		0.290	0.303	0.339	0.315	0.320	0.424		*0.608*		0.332(de)
Crimson clover	Plant yield (kg DM ha^{-1})	23	1632	1688	1846	2172	2213	1941		*0.900*	1915(ab)	
(*Trifolium incarnatum*)	Tissue Cd (mg kg^{-1} DM)		0.048	0.032	0.046	0.057	0.045	0.044		*0.777*		0.045(a)
Strawberry clover	Plant yield (kg DM ha^{-1})	22	1768	1705	2074	2092	1920	1848		*0.666*	1901(ab)	
(*Trifolium fragiferum*)	Tissue Cd (mg kg^{-1} DM)		0.136	0.164	0.131	0.146	0.189	0.143		*0.764*		0.152(abc)
Haresfoot trefoil	Plant yield (kg DM ha^{-1})	14	2400	1909	2300	3781	4192	4109		*0.023*	3115(cd)	
(*Trifolium arvense*)	Tissue Cd (mg kg^{-1} DM)		0.057	0.063	0.068	0.099	0.080	0.087		*0.530*		0.076(abc)
Sheep's burnet	Plant yield (kg DM ha^{-1})	22	1679	1753	1996	1787	2019	1878		*0.917*	1852(ab)	
(*Sanguisorba minor*)	Tissue Cd (mg kg^{-1} DM)		0.159	0.189	0.257	0.140	0.180	0.205		*0.343*		0.188(bc)
Chicory	Plant yield (kg DM ha^{-1})	18	1606	1670	1594	1606	1775	1511		*0.979*	1627(ab)	
(*Cichorium intybus*)	Tissue Cd (mg kg^{-1} DM)		1.520	1.526	1.476	1.958	1.499	1.857		*0.525*		1.639(g)
Plantain	Plant yield (kg DM ha^{-1})	22	1961	2313	2015	2512	2348	2201		*0.781*	2225(ab)	
(*Plantago lanceolata*)	Tissue Cd (mg kg^{-1} DM)		0.701(ab)	0.663(ab)	0.994(b)	0.440(a)	0.709(ab)	0.899(b)		*0.016*		0.734(f)
Kale leaf	Plant yield (kg DM ha^{-1})	9	5200			5091			6391	*0.522*	5146(e)	
(*Brassica oleracea*)	Tissue Cd (mg kg^{-1} DM)		0.128			0.117			0.136	*0.940*		0.123(abcd)
Kale stem	Plant yield (kg DM ha^{-1})	8	1998			2391			2800	*0.468*	2195(abc)	
(*Brassica oleracea)*	Tissue Cd (mg kg^{-1} DM)		0.139			0.137			0.169	*0.787*		0.138(abcd)
Turnip leaf	Plant yield (kg DM ha^{-1})	9	2246			3079			4018	*0.387*	2662(bcd)	
(*Brassica rapa*)	Tissue Cd (mg kg^{-1} DM)		0.546			0.506			1.106	*0.104*		0.526(e)
Turnip bulb	Plant yield (kg DM ha^{-1})	9	3083			5157			5167	*0.101*	4120(de)	
(*Brassica rapa*)	Tissue Cd (mg kg^{-1} DM)		0.248(a)			0.313(ab)			0.494(b)	*0.014*		0.281(cde)
P value											*<0.001*	*<0.001*

*Species mean data excludes superphosphate at 1400 mg kg^{-1} treatment to remove risk of upward bias for turnip and kale

**Mean Olsen-P and total Cd for each superphosphate rate was determined using soil from all replicate pots across all plant species

4.4.3 Plant tissue Cd concentration – effect of plant species

Differences in mean tissue Cd concentration occurred across the plant species assessed in this trial (Table 4.3). Chicory and plantain had greater mean tissue Cd concentrations than all other species (1.639 and 0.734 mg kg^{-1} DM, respectively; Table 4.3 and Figure 4.1).

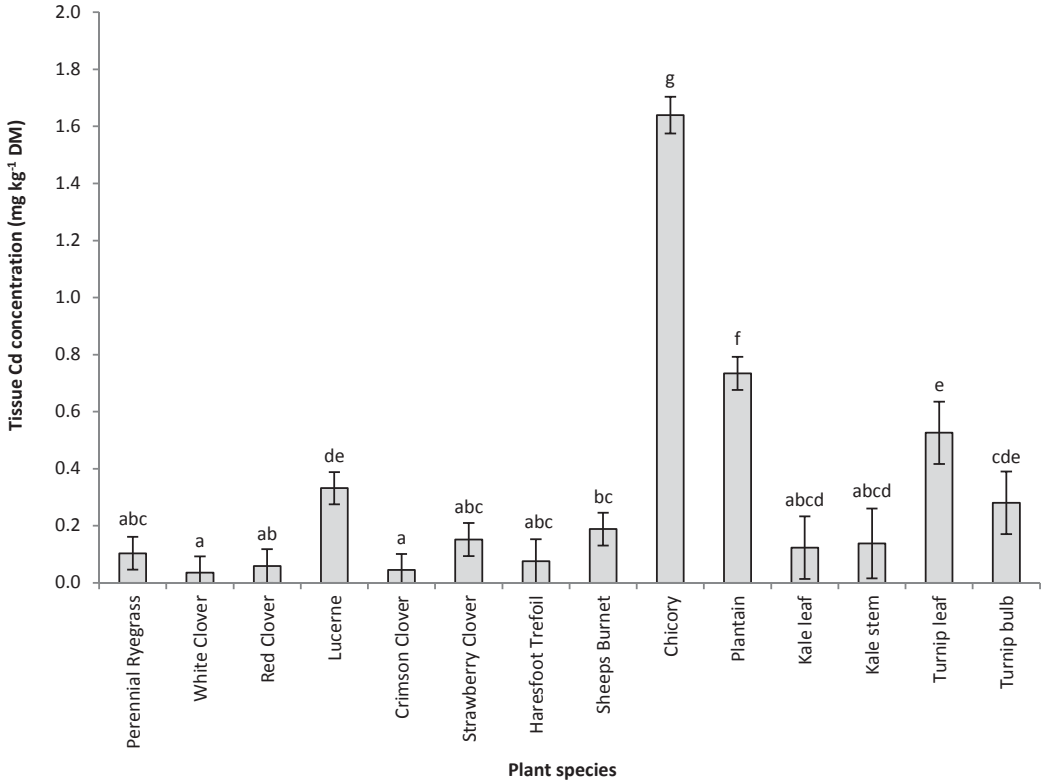

Figure 4.1. Mean tissue Cd concentration for all plant species. Error bars represent the 95% confidence interval. Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

With the exception of lucerne and strawberry clover, the legume species and perennial ryegrass had mean tissue Cd concentrations ranging between just 0.035 and 0.103 mg kg^{-1} DM. Strawberry clover, lucerne, sheep's burnet, kale leaf and stem and turnip leaf and bulb all had moderate tissue Cd concentrations, ranging between 0.152 and 0.526 mg kg^{-1} DM. Therefore, the apparent order of Cd concentration (highest to lowest) in the tested plant species was

chicory > plantain > turnip > lucerne > sheep's burnet > strawberry clover > kale > perennial ryegrass > haresfoot trefoil > red clover > crimson clover > white clover (Table 4.3).

As indicated by the summary in Table 2.10, the absolute and relative tissue Cd concentrations for perennial ryegrass and clover species obtained in this trial are consistent with other glasshouse and field trial datasets generated in New Zealand (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Lee *et al.*, 1996; Loganathan *et al.*, 1997; Gray *et al.*, 1999a, c; Roberts and Longhurst, 2002; Reiser *et al.*, 2014). Gray *et al.* (1999a) reported that the mean tissue Cd concentration of lucerne (~0.45 mg kg^{-1} DM) was around three times greater than that of ryegrass (~0.15 mg kg^{-1} DM) and around four to five times greater than that of white clover (~0.10 mg kg^{-1} DM). Similar trends were reported in this trial, with mean tissue Cd concentrations for lucerne, ryegrass and white clover of 0.332, 0.103 and 0.035 mg kg^{-1} DM, respectively (Table 4.3).

The high mean tissue Cd concentration for chicory and plantain (1.639 and 0.734 mg kg^{-1} DM, respectively) in this trial is an important discovery. Currently, there is little data available regarding Cd accumulation in either chicory or plantain in New Zealand agricultural soils and how this is influenced by variation in soil Cd concentration or soil properties. The limited data that is available (Table 2.10) lacks context, missing either species-specific data (Roberts *et al.*, 1994; Parker *et al.*, 2008), soil Cd data (Crush and Evans, 1990; Parker *et al.*, 2008) or data for other plant species that provides a comparative benchmark for the absolute Cd concentration presented (Crush and Evans, 1990).

Limited research has been undertaken internationally regarding Cd accumulation in chicory or plantain. Abe *et al.* (2008) reported that chicory contained the highest shoot Cd concentration (77 mg kg^{-1} DM) and the highest shoot to root Cd concentration ratio (3.56) of the 93 plant species assessed in their glasshouse trial. In contrast, plantain, perennial ryegrass, white clover and haresfoot trefoil all contained much lower Cd concentrations (5.5, 4.4, 2.7 and 8.0 mg kg^{-1}

DM, respectively) and much lower shoot to root Cd concentration ratios (<0.5). The high Cd concentrations for all plant species in the trial of Abe *et al.* (2008) are likely to be an artefact of the methodology, whereby soil Cd phytoavailability was increased from a background total Cd of 0.17 mg kg^{-1} using cadmium nitrate applied at 3 mg kg^{-1}. This would have created artificially-high soil Cd phytoavailability, relative to that expected under New Zealand agricultural soil conditions.

The high shoot to root Cd concentration ratio for chicory reported by Abe *et al.* (2008) is consistent with the observation by Smolders and Mertens (2012) that members of the Asteraceae family tend to be efficient root-to-shoot Cd translocators. Field data of Martin *et al.* (1996) and Sękara *et al.* (2005) further support this observation, with both studies reporting chicory to have higher Cd concentration in the leaves than the roots. Martin *et al.* (1996) also reported that even at extremely low soil total Cd concentrations (0.004-0.017 mg kg^{-1}) chicory was able to accumulate high leaf Cd concentrations (1.6-2.4 mg kg^{-1} DM). This further indicates the efficiency of this species at extracting Cd from the soil via the root system, and/or subsequently mobilising and transporting it from root to vegetative tissues.

Turnip (*Brassica rapa)* has been shown to be a high Cd accumulator in both field surveys and pot trials (Singh and Nayyar, 1990; De Pieri *et al.*, 1997). De Pieri *et al.* (1997) reported tissue Cd concentrations to be much higher in turnip leaf (0.98-1.2 mg kg^{-1} DM) than bulb (0.17-0.18 mg kg^{-1} DM). Similarly, in this trial, the mean tissue Cd concentration was much higher in the leaf (0.526 mg kg^{-1} DM) than the bulb (0.281 mg kg^{-1} DM). With respect to dietary Cd exposure for livestock grazing a forage turnip crop, the bulb represents a large proportion of the total DM yield and therefore dietary intake (approximately 61% of the total turnip DM yield in this trial). As a consequence, the weighted mean tissue Cd concentration for turnip in this trial was 0.376 mg kg^{-1} DM, slightly higher than that of lucerne (0.332 mg kg^{-1} DM).

Caution needs to be applied in extrapolating results from these international studies to New Zealand agricultural systems, due to differences in soil characteristics, soil Cd levels, sources of soil Cd inputs, and plant cultivars studied. However these studies do provide sound baseline data with regard to relative Cd accumulation in various plant species. In addition, the field data for chicory (Martin *et al.*, 1996; Sękara *et al.*, 2005) and turnips (De Pieri *et al.*, 1997) that was determined at relatively low soil Cd concentrations (similar to that expected in New Zealand agricultural soils) also indicates tissue Cd concentrations that are comparable to those found in this study.

4.4.4 Plant tissue Cd concentration – effect of superphosphate rate and yield

Within each plant species, tissue Cd concentration was generally not influenced by the rate of superphosphate application (Table 4.3) although exceptions occurred in the case of plantain and turnip bulb. Although rate of superphosphate had a significant overall effect on tissue Cd concentration for plantain, tissue Cd concentrations appeared to be highly variable between the different superphosphate rates. While turnip bulb showed a trend for increased tissue Cd concentration with increasing rate of superphosphate, this was only significant at the highest rate of application.

Dilution of plant tissue Cd concentration with increasing plant biomass is a common theme reported within the literature (Mortvedt *et al.*, 1981; Loganathan *et al.*, 1997; Roberts and Longhurst, 2002). However, the data of Mortvedt *et al.* (1981) indicate that soil Cd phytoavailability also has a strong influence on the potential for tissue Cd concentration dilution with increasing biomass. In their study, dilution of Cd concentration in wheat straw occurred when yield was increased using low-Cd (2 mg Cd kg^{-1} P) di-ammonium phosphate (DAP). However, when high-Cd DAP (153 mg Cd kg^{-1} P) was used, straw Cd concentration was maintained or increased.

Similar to the high-Cd DAP scenario of Mortvedt *et al.* (1981), in this study there was little evidence of tissue Cd dilution with increased plant yield. While only haresfoot trefoil gave a significant increase in plant yield with increasing rate of superphosphate, the corresponding tissue Cd concentrations showed no decline. Conversely, there was a trend for the mean tissue Cd concentration of haresfoot trefoil to increase with increasing rate of superphosphate (Table 4.3) although this was not statistically significant. Similarly, in other plant species that indicated non-significant trends for increased yield with increasing rate of superphosphate (i.e. red clover, turnip leaf, turnip bulb) there was no indication of tissue Cd dilution. Furthermore, linear regression analysis (Table 4.4.a) showed a poor coefficient of determination between yield (kg DM ha^{-1}) and tissue Cd concentration (mg kg^{-1} DM) for all plant species (R^2 = <0.001-0.506) with a significant negative relationship between yield and tissue Cd concentration existing only for kale leaf (*P* = 0.032).

Table 4.4. Linear regression coefficients of determination and significance for the relationship between plant Cd concentration (mg kg^{-1} DM) and **a)** plant yield (kg DM ha^{-1}), or **b)** soil total Cd concentration (mg kg^{-1}).

Species	**a)** Plant yield		**b)** Soil total Cd	
	R^2	*P value*	R^2	*P value*
Perennial ryegrass (*Lolium perenne*)	0.009	*0.669*	0.222	*0.027*
White clover (*Trifolium repens*)	0.056	*0.289*	0.082	*0.195*
Red clover (*Trifolium pratense*)	0.028	*0.467*	0.215	*0.039*
Lucerne (*Medicago sativa*)	0.173	*0.054*	0.045	*0.332*
Crimson clover (*Trifolium incarnatum*)	0.003	*0.820*	0.053	*0.291*
Strawberry clover (*Trifolium fragiferum*)	<0.001	*0.945*	0.006	*0.741*
Haresfoot trefoil (*Trifolium arvense*)	0.276	*0.079*	0.004	*0.838*
Sheep's burnet (*Sanguisorba minor*)	0.084	*0.203*	0.007	*0.709*
Chicory (*Cichorium intybus*)	0.026	*0.534*	0.055	*0.382*
Plantain (*Plantago lanceolata*)	0.119	*0.148*	0.013	*0.618*
Kale leaf (*Brassica oleracea*)	0.506	*0.032*	0.031	*0.651*
Kale stem *(Brassica oleracea)*	0.002	*0.910*	0.009	*0.825*
Turnip leaf (*Brassica rapa*)	0.189	*0.242*	0.124	*0.352*
Turnip bulb (*Brassica rapa*)	0.364	*0.085*	0.428	*0.056*

4.4.5 Relationship between soil and plant tissue Cd concentrations

For individual plant species, regression analysis (Table 4.4.b) using individual pot values revealed that soil total Cd concentration was poorly related to tissue Cd concentration (R^2 = 0.006-0.428) with the relationship only significant for perennial ryegrass (*P* = 0.027) and red

clover (P = 0.039). This poor correlation is likely influenced by the relatively narrow range of soil Cd values established by the various rates of superphosphate that were applied, meaning that inherent methodological and analytical error is more likely to mask detection of actual treatment differences.

4.4.6 Implications of this data set for agricultural management

The apparent ability of both chicory and plantain to accumulate high tissue Cd concentration is an important finding because both species are increasingly used as specialist summer forage and livestock finishing crops (Somasiri *et al.*, 2015) and are commonly sown as monoculture stands or in combination with legumes such as white and red clover. Chicory and plantain are valued for their ability to accumulate higher concentrations of essential metals such as cobalt and copper relative to contemporary ryegrass and white clover pastures, thereby increasing the supply of these elements to grazing ruminants (Barry *et al.*, 2001; Harrington *et al.*, 2006; Hoskin *et al.*, 2006). Efficient divalent metal ion absorption and internal transfer mechanisms may allow these plant species to accumulate high levels of copper and cobalt in vegetative tissues, and if non-selective, these same mechanisms could permit the absorption and translocation of Cd^{2+} (Welch and Norvell, 1999).

Although factors such as soil pH, organic matter content and clay mineralogy are known to influence soil sorption-desorption processes and soil Cd solubility (McBride, 1989; Gray *et al.*, 1999c; Loganathan *et al.*, 2012) soil total Cd concentration is considered a key factor regulating Cd phytoavailability (Gray *et al.*, 1999a, c). At 0.43 mg kg^{-1}, the Cd concentration of the Pallic soil used in this trial was similar to the national mean reported by Cavanagh (2014b) for New Zealand agricultural soils (0.44 mg kg^{-1}) but considerably lower than mean soil Cd concentrations for traditionally-intensively farmed regions such as the Waikato (0.74 mg kg^{-1}) and Taranaki (0.70 mg kg^{-1}).

Pallic soils are important to intensive pastoral agriculture in New Zealand, accounting for 12% of New Zealand's total land area; second only to Brown soils at 43% (Landcare Research, 2015). Allophanic soils (5% of New Zealand's land area (Landcare Research, 2015)) that are prevalent in both the Waikato and Taranaki regions are reported to have amongst the highest soil total Cd concentrations of New Zealand pastoral soils (Roberts *et al.*, 1994; McDowell *et al.*, 2013). It is therefore possible that the tissue Cd concentrations determined for chicory and plantain in this trial may be lower than those found on commercial farms (particularly those on Allophanic soils in the Waikato and Taranaki), where these have more greatly enriched soil Cd concentrations than this trial soil.

4.4.6.1 Modelling lamb kidney Cd accumulation

In New Zealand lamb-finishing systems, lambs are typically grazed on high quality ryegrass/white-clover pastures and/or specialist finishing crops so as to maximise daily live weight gain post-weaning ('finishing'). The duration of the finishing period on a pasture and/or forage crop diet can last for several months and is dependent on the rate of live weight gain, which is affected by many factors including the quantity and quality of feed on offer. On pasture, dry matter intake of lambs typically falls within the range 1-1.5 kg DM day^{-1} (Lee *et al.*, 1996) although dry matter intake of chicory has been found to be as high as 2 kg DM day^{-1} (Scales, 1993; Fraser and Rowarth, 1996).

Lee *et al.* (1996) developed algorithms to describe lamb liver and kidney Cd accumulation using data from a grazing study where lambs were fed either low Cd (0.18 +/- 0.08 mg kg^{-1} DM) or high Cd (0.52 +/- 0.17 mg kg^{-1} DM) pasture that was manipulated through the application of cadmium sulphate. This work showed that Cd accumulation in the liver and kidney of grazing lambs was strongly related to daily dietary Cd intake. This would suggest that feeding Cd-rich chicory or plantain as a high percentage of livestock dietary intake has potential to increase Cd accumulation in these tissues. This can be demonstrated by combining the plant tissue Cd

concentration data from this study with the lamb kidney Cd accumulation algorithm (Equation 1) developed by Lee *et al.* (1996):

$$[Cd]_{kidney} = (-205 + 0.981Cd_{intake} + 0.726Time) \div 1000 \qquad (1)$$

where $[Cd]_{kidney}$ refers to kidney Cd concentration (mg Cd kg^{-1} FW), Cd_{intake} represents livestock daily dietary Cd intake (µg Cd day^{-1}), and *Time* is the period (days) over which livestock are exposed to this daily dietary Cd intake.

Using Equation 1 with the variables listed in Table 4.5, lambs with a feed intake of 1 kg DM $lamb^{-1}$ day^{-1} for 60 days are predicted to have kidney Cd concentrations of 1.45 and 0.82 mg kg^{-1} FW, when finished on Cd-rich chicory monoculture (1.639 mg kg^{-1} DM) and chicory-white clover mixed forage (0.997 mg kg^{-1} DM), respectively (Table 4.5). In comparison, little change in kidney Cd concentration is predicted when lambs are finished on low-Cd (0.086 mg kg^{-1} DM) ryegrass-white clover pasture. The predicted kidney Cd concentration for lambs grazing a pure chicory stand in this scenario exceeds the current European Commission (EC) food standard ML of 1.0 mg kg^{-1} FW (EC, 2014), although it meets the current New Zealand ML of 2.5 mg kg^{-1} FW (FSANZ, 2011).

Table 4.5. Variables used in determining kidney Cd concentration for lambs finished on different forages, using the equation of Lee *et al.* (1996).

	Chicory monoculture forage stand		Chicory - white clover forage stand		Perennial ryegrass - white clover pasture	
Cd concentration in chicory (mg Cd kg^{-1} DM)	1.639		1.639		-	
Cd concentration in ryegrass (mg Cd kg^{-1} DM)	-		-		0.103	
Cd concentration in white clover (mg Cd kg^{-1} DM)	-		0.035		0.035	
Proportion of chicory in sward (%)	100%		60%		-	
Proportion of perennial ryegrass in sward (%)	-		-		75%	
Proportion of white clover in sward (%)	-		40%		25%	
Cd concentration in diet (mg Cd kg^{-1} DM)	1.639		0.997		0.086	
Daily feed intake (kg DM $lamb^{-1}$ day^{-1})	1.0	1.5	1.0	1.5	1.0	1.5
Cd_{intake} (µg day^{-1})	1639	2459	997	1496	86	129
Time (days)	60	30	60	30	60	30
$[Cd]_{kidney}$ (mg Cd kg^{-1} FW)	*1.45*	*2.23*	*0.82*	*1.28*	*-0.08*	*-0.06*

Increasing chicory monoculture and chicory-white clover mixed forage intake to 1.5 kg DM $lamb^{-1}$ day^{-1} but using a shorter grazing period (30 days) results in an increase in the predicted

kidney Cd concentrations to 2.23 and 1.28 mg kg^{-1} FW, respectively (Table 4.5), indicating the models sensitivity to daily dietary Cd intake. In both cases, these kidney Cd concentrations are still below the New Zealand ML but well in excess of the EC ML.

In comparison, Reiser *et al.* (2014) recently modelled livestock liver / kidney Cd accumulation using pasture Cd data from a range of locations in New Zealand. They reported that daily intake of Cd exceeded acceptable levels with regard to offal food standards only in a small number of cases (<10%), with the authors citing consistency with abattoir offal survey data reported by Roberts *et al.* (1994). However, the Cd concentrations in the predominantly ryegrass-white clover pasture dataset of Reiser *et al.* (2014) (Table 2.10) are much lower than that found for chicory and plantain in this study. As such, their modelled exceedance does not reflect the risk where stock are intensively grazed on these higher Cd forages. In addition, chicory and plantain were not commonly used as specialist forages at the time of the abattoir survey of Roberts *et al.* (1994) hence this offal Cd dataset may not reflect the current situation.

As edible offal has an export value of NZ$211 million (MIA, 2015), potential exceedance of food standard MLs has an economic consequence. Currently, kidneys from animals greater than 30 months of age are discarded from trade for human consumption to avoid exceedance of food standard MLs (MAF, 2008). However, the data from this trial supports observations that MLs may potentially be exceeded in livestock younger than 30 months, where intensive grazing of Cd-rich forage occurs (Lee *et al.*, 1994; Loganathan *et al.*, 1999).

4.4.6.2 Use of soil total Cd for Cd risk management

Soil total Cd concentration may be suitable for managing on-going soil Cd accumulation under the existing TFMS. However, the findings from this trial emphasise that soil total Cd concentration alone is unlikely to be adequate for managing risks related to plant accumulation and Cd transfer to the human diet. This is evident by the large variation in plant tissue Cd concentrations that occurred across the twelve plant species assessed in this pot

trial, despite all species being grown under the same soil conditions. There is a lack of data for many forage species to demonstrate that a clear relationship exists between plant tissue Cd concentration and soil total Cd concentration, and further to this, what influence other soil factors (e.g. soil pH, organic matter content and clay mineralogy) may have on this relationship.

It is advised that field research is undertaken to test the concept, developed from this glasshouse trial, that field grown chicory and plantain will have high tissue Cd concentrations in soils with high Cd status derived from long-term P fertiliser use. Field data for chicory and plantain is also required across a diverse range of sites to determine whether relationships exist between plant tissue Cd concentration and soil factors that influence Cd phytoavailability (e.g. total Cd concentration, soil pH and organic matter content). This information is required to more accurately model Cd accumulation in ruminant livestock, and for developing farm-specific management plans aimed at minimising animal Cd accumulation.

4.5 Conclusions

Large differences in plant tissue Cd concentration occurred across the 12 forage species assessed in this study. Chicory and plantain had markedly greater mean tissue Cd concentrations than all other plant species, at 1.639 and 0.734 mg kg^{-1} DM, respectively. In comparison, perennial ryegrass and white clover, which have traditionally formed the basis of New Zealand's pastoral industry, had mean tissue Cd concentrations of 0.103 and 0.035 mg kg^{-1} DM, respectively. Based on this data, an animal accumulation model (Lee *et al.*, 1996) predicted rapid kidney Cd accumulation with exceedance of the EC food standard ML (1.0 mg kg^{-1} FW) occurring over a 30-60 day grazing period for lambs fed Cd-rich (1.639 mg kg^{-1} DM) chicory monoculture. In contrast, lamb kidney Cd concentration was predicted to remain virtually unchanged over the same period when grazing low Cd (0.086 mg kg^{-1} DM) ryegrass-white clover pasture. With increased integration of chicory and plantain into livestock grazing

systems, increased dietary Cd intake may result in livestock kidney and liver exceeding food standard MLs well in advance of the current New Zealand meat industries 30-month animal offal discard age.

CHAPTER 5 : Field survey of cadmium concentrations in chicory, plantain, ryegrass and white clover

This chapter (together with Chapter 4) was summarised in an oral presentation at the 2016 Fertiliser and Lime Research Centre conference. Citation:

Stafford, A., Anderson, C., Hedley, M., McDowell, R., 2016. Cadmium accumulation in forage species used in New Zealand livestock grazing systems. In: Integrated nutrient and water management for sustainable farming. (Eds L.D. Currie and R.Singh). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 10 pages.

5.1 Abstract

A field survey was carried out across 30 New Zealand pastoral farms (23 dairy and 7 sheep & beef) with varying land-use history and soil characteristics to evaluate cadmium (Cd) concentration ranges for chicory (*Cichorium intybus*), plantain (*Plantago lanceolata*), ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*). Soil samples collected at each plant tissue sampling site were used to derive relationships between tissue Cd concentration with soil total Cd, pH and total carbon content. Species-mean tissue Cd concentrations decreased in the order chicory (1.820 mg kg^{-1} DM) > plantain (0.803 mg kg^{-1} DM) > ryegrass (0.114 mg kg^{-1} DM) > white clover (0.074 mg kg^{-1} DM). Tissue Cd concentrations ranged greatly for chicory (0.40-4.50 mg kg^{-1} DM) and plantain (0.23-2.40 mg kg^{-1} DM) whereas there was little variation for ryegrass and white clover (all samples <0.3 mg kg^{-1} DM). However, only the variation in tissue Cd concentration for chicory could be satisfactorily explained (R^2 = 0.745) by the variables soil total Cd concentration, pH and total carbon content. The data from this field survey validates the high tissue Cd concentrations observed for chicory and plantain in a previous glasshouse trial discussed in Chapter 4.

5.2 Introduction

Ruminant-grazed pastoral systems represent the predominant agricultural land use in New Zealand, accounting for approximately 12 million hectares (StatsNZ, 2013) and approximately 40% of total export earnings (Treasury, 2016). Because of the importance of livestock grazing systems to New Zealand's economy, considerable research into Cd accumulation and cycling within these systems occurred during the 1990's, amid greater awareness of soil Cd accumulation as a long-term management concern (Bramley, 1990). This research found that ingested Cd was not expressed in significant quantities in either meat or milk products (Solly *et al.*, 1981; Sharma *et al.*, 1982; Morrison, 1988). However, despite the majority (over 99%) of ingested Cd being excreted (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) Cd was found to accumulate in the liver and kidney of livestock due to high levels of metallothionein synthesis in these tissues, with tissue Cd concentration increasing with age (Lee *et al.*, 1994; Lee *et al.*, 1996). To minimise the risk of food standard Cd maximum level (ML) exceedances for these offal products, the New Zealand meat industry introduced restrictions on the trade of ruminant liver and kidney for human consumption to animals aged 30 months or less (MAF, 2008).

However, in addition to liver / kidney tissue Cd concentration increasing with increasing age, the rate of Cd accumulation was also found to be greatest in young stock within the first few month of weaning (Lee *et al.*, 1994; Lee *et al.*, 1996). Further to this, liver/kidney Cd accumulation rate was found to increase with increasing dietary Cd intake (Lee *et al.*, 1994; Lee *et al.*, 1996; Loganathan *et al.*, 1999). Although soil ingestion contributes to livestock dietary Cd intake, it was determined that the majority (approximately 90%) of total dietary Cd intake occurs via the forage these animals consume (Lee *et al.*, 1996; Roberts and Longhurst, 2002). As a consequence, grazing young stock on Cd-rich forages may result in more rapid

kidney/liver Cd accumulation, potentially leading to more frequent exceedance of food standard maximum levels (MLs) (Loganathan *et al.*, 1999).

The majority of research in New Zealand on animal forages has historically focussed on ryegrass and white clover based pastures (Table 2.10). Cadmium concentrations in these pasture species has been found to be relatively low (typically <0.3 mg kg^{-1} DM) with Cd concentrations greater in grasses than legumes (Roberts *et al.*, 1994; Loganathan *et al.*, 1997; Gray *et al.*, 1999a, c; Reiser *et al.*, 2014). However, since many of these studies were undertaken, there was been significant diversification in the forage species used in New Zealand livestock grazing systems, for which there is no documented information on Cd accumulation. Generating this data is seen as vital for improving animal Cd accumulation risk assessment models (Reiser *et al.*, 2014).

To build this dataset, an initial glasshouse trial was undertaken to benchmark Cd accumulation in 12 common forage plant species (Stafford *et al.*, 2016). This study revealed that chicory and plantain in particular contained very high mean tissue Cd concentrations (1.639 and 0.734 mg kg^{-1} DM, respectively). In comparison, ryegrass and white clover had mean tissue Cd concentrations of only 0.103 and 0.035 mg kg^{-1} DM, respectively. The high tissue Cd concentrations for chicory and plantain reported by Stafford *et al.* (2016) is potentially an important finding, since both of these plant species are increasingly being sown as specialist lamb finishing crops, and also to provide high quality forage over the hot, dry summer and early autumn period when ryegrass/white clover based pastures typically struggle.

Even though the study by Stafford *et al.* (2016) provides a useful benchmark regarding relative Cd accumulation in different forage species by means of glasshouse trial, extrapolation is limited in that it only represents Cd accumulation data for a single soil, under artificial (homogenised, regularly irrigated) conditions, which may not represent what occurs in situ. As soil total Cd concentration, pH, organic matter and clay mineralogy are considered important

factors that influence Cd phytoavailability (McBride, 1989; McBride *et al.*, 1997; Naidu *et al.*, 1997; Gray *et al.*, 1998, 1999c, d; Loganathan *et al.*, 2012) there is a need to quantify how variation in these factors influences tissue Cd concentration in chicory and plantain, given the apparent ability of these plant species to accumulate Cd. Therefore, a field survey was undertaken to quantify the accumulated tissue Cd concentrations in chicory, plantain, ryegrass and white clover, and to identify the soil factors affecting Cd uptake using a range of New Zealand dairy and sheep & beef farms with different soil characteristics (7 different soil orders were represented), and differences in P fertiliser and other land management history.

5.3 Methodology

A field survey of pastures and crops on 30 commercial pastoral farming operations (22 North Island, 8 South Island) was undertaken during early summer (December) of 2014. Figure 5.1 indicates the locations of the sites sampled in this survey. Often, more than one sampling site was located within a property, where large difference in land use history or soil type was evident. Table 5.1 summarises the number of samples (by plant species) taken by soil order, while Table 5.2 summarises land use history of the individual sampling sites.

Table 5.1. Summary of field survey sampling sites by plant species and soil order (separated into North and South Island sites).

Soil order	Plant species				*Total*
	Chicory	Plantain	Ryegrass	White clover	
North Island					
Allophanic	18	11	15	5	*49*
Pumice	4	7		11	*22*
Organic	3	3	2	4	*12*
Gley		1		1	*2*
South Island					
Pallic	3	3	2	2	*10*
Brown	2	3		3	*8*
Recent		1		1	*2*
Gley		1	1		*2*
Total	*30*	*30*	*20*	*27*	*107*

Table 5.2. Summary of field survey sampling sites by plant species and land use history.

Land use		Plant species				*Total*
Current*	Historic**	Chicory	Plantain	Ryegrass	White clover	
Dairy	Dairy	20	10	14	10	54
Dairy Goat	Dairy	2	2	1	1	6
Dairy	Potatoes, Beef	0	1	1	0	2
Dairy	Maize	1	0	1	0	2
Dairy	Forestry	2	2	0	4	8
Dairy	Sheep / Beef	3	5	3	3	14
Sheep / Beef	Sheep / Beef	2	10	0	9	21
Total		*30*	*30*	*20*	*27*	*107*

* Land use over the last 5-10 years, ** Land use in the previous 10-20 years.

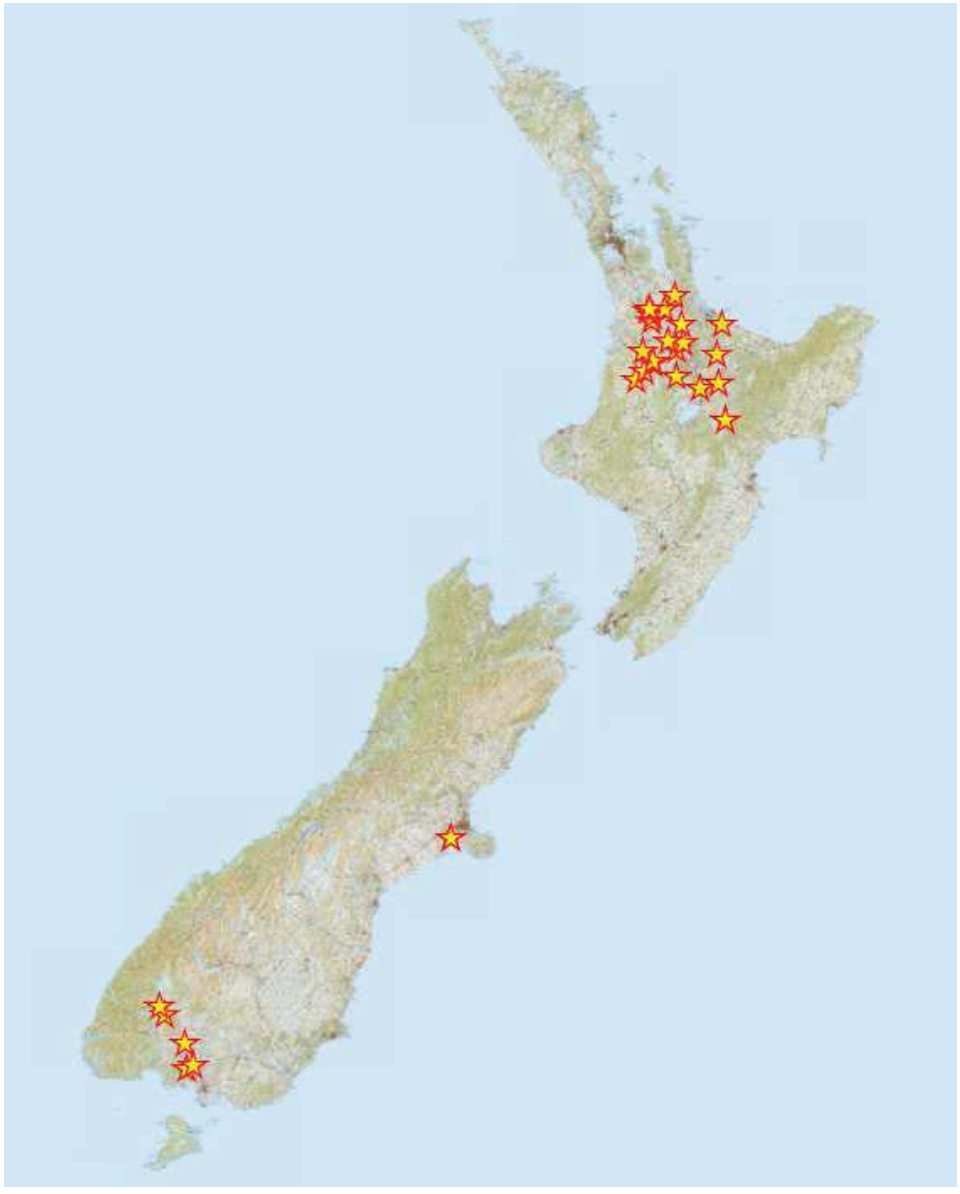

Figure 5.1. Geographic overview of sampling sites used in the field survey**.**

5.3.1 Sampling methodology

Plant tissue samples and soil samples were collected at each sampling location. Where possible, chicory or plantain was referenced against ryegrass or white clover from the same paddock (e.g. in the case of plantain / chicory / white clover forage stand, or in a pasture also containing plantain or chicory). In the case of pure chicory or plantain forage stands where this was not possible, a ryegrass or white clover sample (and associated soil sample) was collected from an adjacent pasture on the same soil type, with similar management history.

Five sub-sampling locations were selected within each site, located within representative, consistent areas of the paddock. Care was taken to avoid obvious changes in soil type, topography, farm infrastructure or paddock features (e.g. natural camp sites, troughs, hedges etc.) that would be likely to induce avoidable variation between sub-samples. For chicory and plantain tissue samples, 2-3 plants were harvested with shears approximately 3 cm above the soil surface at each sub-sampling site, avoiding plants with any soil contamination. Chicory and plantain plants were harvested near to grazing maturity (vegetative growth, approximately 25-30 cm in height). Ryegrass / white clover samples were harvested with shears at approximately 3 cm above the soil surface, with 3 tissue sampling ‘strips’ at each sub-sampling site. Three soil cores were extracted at each sub-sampling site, taken immediately adjacent to the harvested plants (chicory/plantain) or within the harvest strip (ryegrass/white clover). Soil samples were collected to 150 mm soil depth, except at one site (a Recent soil in Southland) where this was not possible due to the stoniness of the soil. At this site, 75 mm soil cores were collected. Plant tissue and soil samples from each subsampling site were aggregated (i.e. 10-15 plant samples or 15 soil sores) providing a single plant tissue or soil sample for each site.

5.3.2 Chemical analysis

5.3.2.1 Plant tissue Cd

All plant tissue samples collected during the field survey were dried in their paper bags at 60°C for 3 days. Subsequently, these samples were then ground, before being subsampled (0.2 g) for total Cd analysis following microwave digestion (Anderson, 1996). Briefly, 0.2 g subsamples were weighed into microwave digestion vessels into which 2 mL of 30% hydrogen peroxide and 1 mL of concentrated nitric acid were added. Vessels were then capped and placed in a CEM MARS Xpress microwave digester, with temperature ramped up to 210°C over 24 minutes, and then held at 210°C for a further 30 minutes. Once cooled, digests were topped up to 20 mL with deionised water and vortex-mixed. These were then centrifuged and filtered, before 3mL aliquots were extracted, diluted as necessary using 5% nitric acid, and analysed for total Cd using a Perkin-Elmer NEXION 300D Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS). The limit of detection (LOD) for Cd using this methodology was 0.02 mg kg^{-1} (F. Calvert, personal communication, July 1, 2014). For quality control purposes, two blanks and one standard reference material (National Institute of Standards and Technology [NIST] 1515; apple leaves) were included within every 40 sample batch. The acceptable Cd-recovery working range for this standard reference material is 95-105% (F. Calvert, personal communication, September 28, 2016). To correct for instrument drift, calibration rescale occurred every 20 samples.

5.3.2.2 Soil total Cd, total C and pH

Analytical methodology is provided in Chapter 3 for the assessment of soil total Cd (Section 3.4.4.1), soil total C (Section 3.4.4.3) and soil pH (Section 3.4.4.5).

5.3.3 Statistical analysis

Statistical analysis was carried out using the software SPSS (IBM Corp, 2013). Analysis of variance (ANOVA) tests were undertaken to identify whether significant differences existed between treatments overall. Tukeys honestly significant difference (HSD) was then run as a post-hoc analysis to identify individual treatment means that were different at $P < 0.05$. As the Recent soil order was represented by only one sample this group was excluded from the statistical analysis of soil properties by soil order. A set of simple linear correlation analysis relating the plant tissue Cd concentration to soil total Cd concentration was performed. Stepwise regression using backwards elimination was used to determine overall relationships between soil total Cd concentration, pH and total C content on the plant tissue Cd concentration. Independent variables were individually removed from the regression model when $P > 0.1$.

5.4 Results and discussion

5.4.1 Soil characteristics of survey sites

Soil total Cd, pH and total C data for the field survey sampling sites is summarised in Table 5.3. As the majority of survey sites were located in the Waikato, Bay of Plenty and Central Plateau regions, Allophanic, Pumice and Organic soil orders represented the majority of soil orders. Overall, significant ($P < 0.001$) differences in mean soil total Cd concentration (mg kg^{-1}) occurred between soil orders, with the greatest mean soil total Cd concentrations occurring in the Allophanic and Organic soil orders (0.98 and 0.72 mg kg^{-1}, respectively). However, pairwise comparison revealed that only the mean Cd concentration of the Allophanic soil order was significantly ($P < 0.05$) greater, relative to that of the Brown, Grey and Pallic soil orders (0.32, 0.30 and 0.19 mg kg^{-1}, respectively). The greater Cd concentrations of the Allophanic soil order is consistent with previous research (Roberts *et al.*, 1994; McDowell *et al.*, 2013; Cavanagh, 2014b) and likely reflects the traditionally intensive land use and greater P fertiliser inputs into

these soils over time (Bramley, 1990; Roberts *et al.*, 1994). The Allophanic soil order also had by far the greatest range in soil total Cd concentrations (0.49-2.10 mg kg^{-1}) indicating varied land use and P fertiliser management history.

Table 5.3. Summary of soil characteristics for sampling sites used in the field survey (150 mm sampling depth).

		Soil order							*P* value
		Gley	Allophanic	Organic	Pumice	Brown	Pallic	Recent*	
	n	2	24	9	12	4	4	1	
Total Cd (mg kg^{-1})	Mean	0.30(a)	0.98(b)	0.72(ab)	0.46(ab)	0.32(a)	0.19(a)	0.39	*<0.001*
	Min	0.22	0.49	0.50	0.19	0.26	0.16		
	Max	0.37	2.10	1.10	0.72	0.46	0.22		
pH	Mean	5.60	5.53	5.50	5.64	5.60	5.65	5.50	*0.846*
	Min	5.60	5.20	5.00	5.00	5.50	5.40		
	Max	5.60	6.00	6.00	6.60	5.70	5.80		
Total C (%)	Mean	4.10(a)	8.98(a)	21.14(b)	5.84(a)	8.75(a)	2.58(a)	11.00	*<0.001*
	Min	4.00	3.10	13.20	3.10	8.10	2.20		
	Max	4.20	15.30	38.20	7.90	9.40	3.40		

*Excluded from statistical analysis due to their only being one sample representing this soil order

There was no difference (P = 0.846) in soil pH between soil orders (Table 5.3), which is not surprising given soil pH is a product of farm / soil fertility management rather than an inherent soil property. The mean soil pH levels ranging between 5.50-5.65 across all soil orders is slightly lower than the optimum range for pastoral production on mineral soils of 5.8-6.0 (Roberts and Morton, 2009) that is assessed at a standard depth of 75 mm. This likely reflects the greater soil sampling depth (150 mm) used in this trial, since surface application of lime has limited effect on pH deeper in the soil profile (Wheeler, 1997; Wheeler and O'Connor, 1998; Moir and Moot, 2014). There was however, a large range in soil pH within each of the Allophanic (5.2-6.0), Organic (5.0-6.0) and Pumice (5.0-6.6) soil orders that formed the majority of the survey sites. This range in soil pH was desired within the survey sites, given pH is considered to be one of the most important factors regulating Cd phytoavailability in variable charge soils (Bolan *et al.*, 2003c; Loganathan *et al.*, 2012; Young, 2012).

Significant (P <0.001) differences in mean total C content occurred between soil orders (Table 5.3), although pairwise comparison revealed that the only significant differences occurred for the Organic soil order, which had greater (P < 0.05) mean total C (21.14%) than all other soil

orders (ranging between 2.58-11%). Although not significant, there was a trend for mean total C content to be greater in the Allophanic and Brown soil orders (8.98 and 8.75%, respectively) than the Pumice, Gley and Pallic soil orders (5.84, 4.10 and 2.58%, respectively). Soil total C was the most variable (13.2-38.2%) in the Organic soil order, likely reflecting different stages of soil development (O'Connor *et al.*, 2001).

The importance of soil total Cd concentration, soil organic matter / carbon and soil pH in regulating soil Cd sorption processes, solubility and plant Cd uptake has been well documented in previous research (McBride *et al.*, 1997; Gray *et al.*, 1998, 1999d; McBride, 2002). For example, across a range of New Zealand soils, Gray *et al.* (1999d) reported that these three factors combined explained 85% and 76% of the variation in soil Cd desorption and soluble Cd concentration between different soils, respectively. Although Cd phytoavailability is expected to increase with increasing soil total Cd concentration, this can be offset by increases in soil organic matter since this increases the soils Cd sorption potential, or increases in soil pH since this favours increased specific-sorption of Cd (Christensen and Haung, 1999; Loganathan *et al.*, 2012). For these reasons, soil Cd phytoavailability is also likely to vary between soils of similar total Cd concentration, where the soils differ in pH and organic matter content (particularly where soil pH and organic matter content are correspondingly low or high in tandem).

5.4.2 Plant tissue Cd concentration ranges

Differences in mean tissue Cd concentration for the various plant species were strongly significant overall ($P < 0.001$; Figure 5.2). Comparisons between individual plant species revealed that the mean tissue Cd concentration of chicory (1.82 mg kg^{-1} DM) was significantly greater ($P < 0.05$) than that of plantain (0.80 mg kg^{-1} DM) which in turn was significantly greater ($P < 0.05$) than that of ryegrass (0.11 mg kg^{-1} DM) and white clover (0.07 mg kg^{-1} DM). Mean Cd concentrations of the latter two species were not significantly different ($P > 0.05$). The mean tissue Cd concentrations for ryegrass and white clover determined in this field

survey are very similar to those previously reported for grasses and legumes in New Zealand (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Lee *et al.*, 1996; Loganathan *et al.*, 1997; Roberts and Longhurst, 2002; Reiser *et al.*, 2014). Notably, Roberts *et al.* (1994) reported from a field survey of 312 regularly-fertilised pastoral farms that the mean tissue Cd concentration was greater for grasses (0.10 mg kg^{-1} DM) than legumes (0.06 mg kg^{-1} DM). In absolute and relative terms, the Cd concentration for ryegrass and white clover in this survey (0.11 and 0.07 mg kg^{-1} DM, respectively) was remarkably consistent with the findings of Roberts *et al.* (1994).

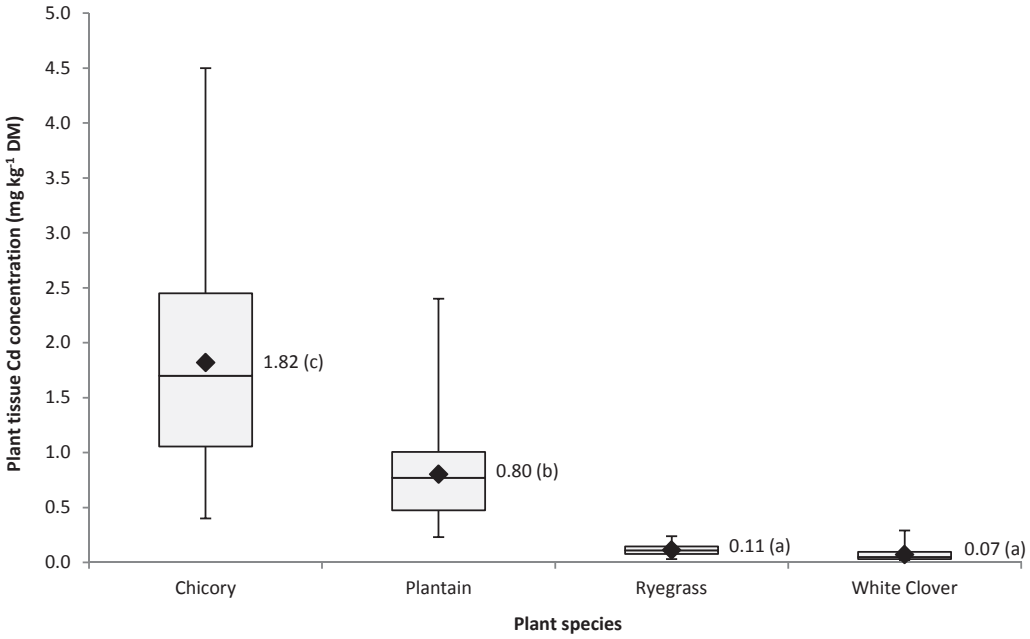

Figure 5.2. Tissue Cd concentration ranges for chicory, plantain, ryegrass and white clover across the survey sites. Box and whisker plots represent data quartiles. Black diamond and associated value represent the mean tissue Cd concentration for each plant species. Means with the same letter indicate differences are not significant from one another (P <0.05).

Few relevant studies exist to contrast the chicory and plantain tissue Cd data from this survey against. Field data from two acidic (pH 5.1-5.2), low organic matter (1.1-1.4%) sandy soils in South Carolina (USA) showed high chicory leaf Cd concentrations (1.6 and 2.4 mg kg^{-1} DM) under 'uncontaminated' soil conditions, with the authors (Martin *et al.*, 1996; Simon *et al.*, 1996) noting the potential of chicory as a potential Cd-phytoindicator species. Unfortunately, soil total Cd concentration was not provided by the authors, with only double-acid (0.05 M HCl

+ 0.025 M H_2SO_4) extractable soil Cd concentrations being reported for the two soils. Similarly, Crush and Evans (1990) reported a high mean tissue Cd concentration (3 mg kg^{-1} DM) for chicory grown under glasshouse conditions in a New Zealand Pallic soil with 'little or no P fertiliser history'. Unfortunately, again no soil Cd concentration data was provided by the authors. However, both of these studies support the data from this study in suggesting that chicory can accumulate relatively high tissue Cd concentrations even at relatively low 'uncontaminated' soil Cd concentrations. Lastly, Parker *et al.* (2008) reported high tissue Cd concentrations for a mixed chicory/plantain/red clover/white clover forage stand (0.361-0.754 mg kg^{-1} DM) relative to an adjacent ryegrass/white clover pasture (0.110-0.224 mg kg^{-1} DM). However, this study did not discuss species-specific data or soil Cd data, although it was noted the site (a New Zealand Pallic soil) had 'a long history of annual superphosphate applications'.

Clearly evident in Figure 5.2 is the large range in plant tissue Cd concentrations for both chicory (0.40-4.50 mg kg^{-1} DM) and plantain (0.23-2.40 mg kg^{-1} DM). In contrast, ryegrass and white clover exhibited only narrow variation in tissue Cd concentration, with all tissue Cd concentrations for both species being below 0.3 mg kg^{-1} DM. The differences in Cd accumulation between chicory, plantain, ryegrass and white clover illustrates relative differences between these species in their ability to either; i) extract Cd from different soil fractions of varying bond-strength/lability, ii) transfer Cd from soil solution across the root membrane, or iii) subsequently remobilise and transfer Cd from the root to above ground vegetative tissues (Welch and Norvell, 1999). As plant tissue was only sampled at 30 mm above ground level (to approximate animal grazing intake) the necessary data is not available within this study to explore the relative importance of these mechanisms for explaining the inter-species variation in vegetative-biomass Cd concentrations.

Internal root-to-shoot translocation efficiency is, however, considered to be a key factor dictating Cd expression in above ground tissues (Florijn and Van Beusichem, 1993; Welch and Norvell, 1999; Uraguchi *et al.*, 2009). Notably, species within the Leguminosae and Gramineae

families tend to be shoot Cd excluders (Smolders and Mertens, 2012) explaining the low tissue Cd concentrations for ryegrass and white clover in Figure 5.2. In contrast, species within the Asteraceae family tend to be efficient root-to-shoot Cd translocators (Smolders and Mertens, 2012), which is consistent with the high vegetative tissue Cd concentrations for chicory in this study. The high internal Cd translocation efficiency of chicory was demonstrated by Martin *et al.* (1996) who reported tissue Cd concentrations to descend in the order leaf > crown > stem > root. Greater tissue Cd concentrations in leaf than root tissues of chicory have also been reported by Simon *et al.* (1996), Sękara *et al.* (2005) and Abe *et al.* (2008). This indicates that very high internal Cd translocation efficiency is a key factor explaining the ability of chicory to accumulate the high tissue Cd concentrations as observed in this study. This is a potential area for further research, with potential to lead to plant breeding opportunities to manage Cd accumulation in the above ground vegetative tissue of chicory and plantain.

The mean tissue Cd concentrations for chicory, plantain, ryegrass and white clover in this field survey (1.820, 0.803, 0.114 and 0.074 mg kg^{-1} DM, respectively) are consistent with the mean tissue Cd concentrations generated in the previous glasshouse trial (1.639, 0.734, 0.103 and 0.035 mg kg^{-1}, respectively; Stafford *et al.* (2016)). This field survey therefore validates the high tissue Cd concentrations observed for chicory and plantain in the initial glasshouse trial. It also supports the hypothesis stemming from animal Cd accumulation risk assessment modelling (Stafford *et al.*, 2016) that grazing young stock on high-Cd chicory or plantain forage stands has the potential to increase kidney/liver Cd accumulation rate, with the consequence of possible exceedance of food standard MLs prior to the New Zealand meat industry 30-month offal-discard age. Although historic work indicates that the majority (99%) of ingested Cd is excreted (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) and that little ingested Cd finds its way into milk or meat products (Solly *et al.*, 1981; Sharma *et al.*, 1982; Morrison, 1988), currently little data exists to prove this for Cd-rich chicory / plantain crops, which are

increasing being used as specialist summer-autumn forages for dairy cattle. It is recommended that this is an area for further research.

5.4.2.1 Relationship of plant tissue Cd concentration to soil variables

5.4.2.1.1 Soil total Cd as a single variable

The relationship between plant tissue Cd concentration and soil total Cd concentration for each plant species is shown in Figure 5.3, with soil order identified for each sample. Significant positive correlations were evident for chicory ($P < 0.001$; Figure 5.3.a), plantain ($P = 0.013$; Figure 5.3.b) and ryegrass ($P = 0.032$; Figure 5.3.c), although the coefficient of determination was very weak for plantain and ryegrass ($R^2 = 0.2$ and 0.23, respectively) indicating that total Cd alone accounted for little of the variation in tissue Cd concentration for these two species. In contrast, soil total Cd alone explained approximately 55% of the variation in tissue Cd concentrations for chicory. No relationship was evident between white clover tissue Cd concentration and soil total Cd concentration (Figure 5.3.d). The finding for ryegrass is consistent with that of Reiser *et al.* (2014) who reported only a weak correlation between soil total Cd and tissue Cd concentration in ryegrass-dominant pastures. Similarly, Roberts et al. (1994) reported a small but significant increase in tissue Cd concentration for grasses, but no difference for legumes, in samples collected from Cd-enriched pastoral sites relative to native (non-P fertilised) sites.

It is likely that there will be a greater chance of establishing a stronger relationship between soil and plant Cd concentrations when a greater range in soil total Cd concentration exists. Analysis of upper and lower quartile soil total Cd concentration ranges for each plant species (Table 5.4) revealed that the absolute difference (mg kg^{-1}) between the mean Cd concentration within the upper and lower quartile ranges descended in the order ryegrass (1.03 mg kg^{-1}) >

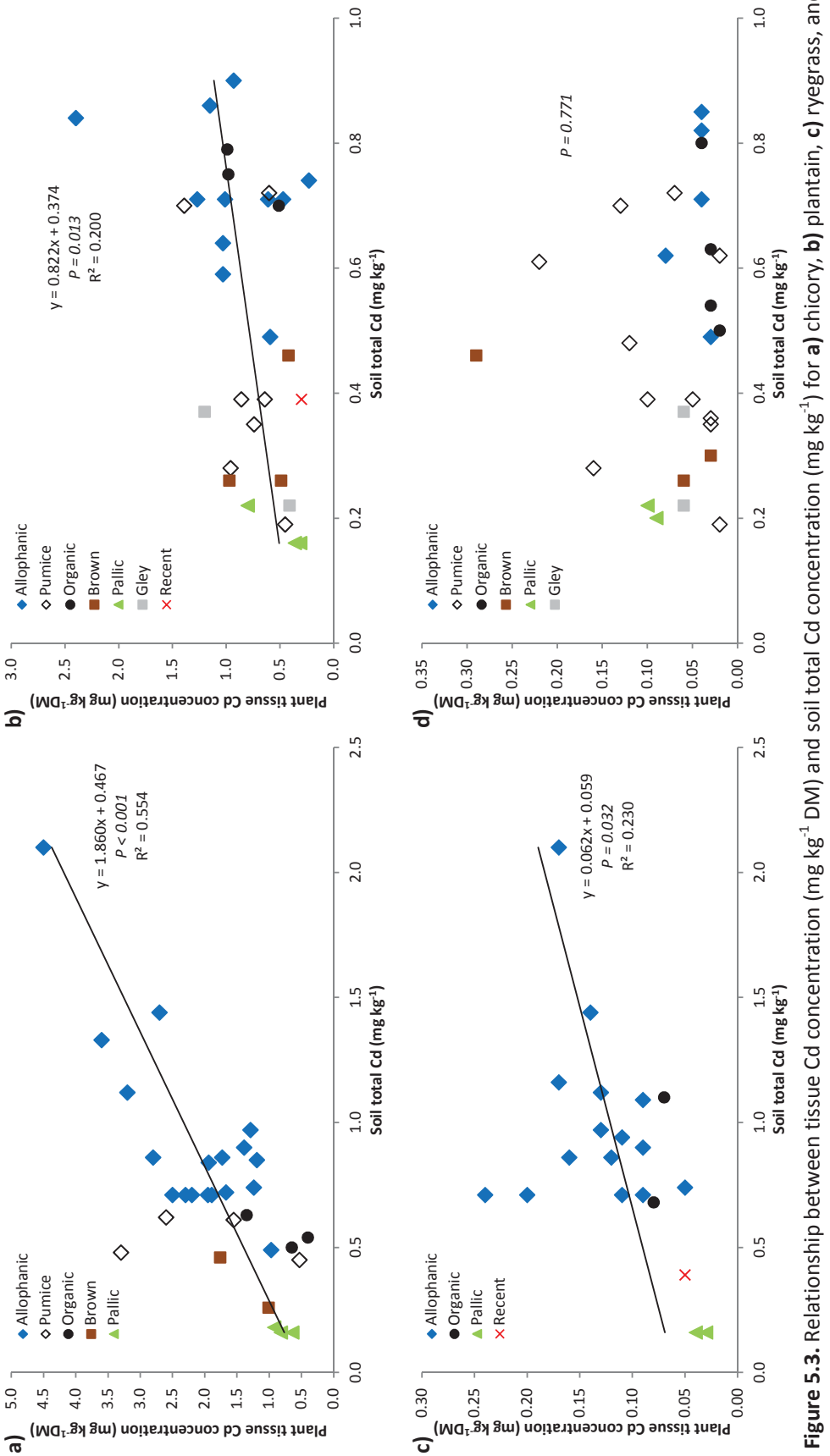

Figure 5.3. Relationship between tissue Cd concentration (mg kg^{-1} DM) and soil total Cd concentration (mg kg^{-1}) for **a)** chicory, **b)** plantain, **c)** ryegrass, and **d)** white clover.

chicory (0.87 mg kg^{-1}) > plantain (0.58 mg kg^{-1}) > white clover (0.51 mg kg^{-1}). Therefore, variation in the range of soil total Cd concentrations at survey sites for the different plant species does not explain the strength of the relationship between soil and plant Cd concentration.

Table 5.4. Soil total Cd concentration (mg kg^{-1}) upper quartile and lower quartile ranges, mean Cd concentrations within these quartile ranges, and the difference between the mean soil Cd concentration within each of the upper and lower quartile ranges, by plant species.

		Chicory	Plantain	Ryegrass	White clover
Lower quartile	Range	0.16 - 0.49	0.16 - 0.30	0.16 - 0.71	0.19 - 0.33
	Mean	0.33	0.22	0.35	0.24
Upper quartile	Range	0.86 - 2.10	0.71 - 0.90	1.09 - 2.10	0.63 - 0.85
	Mean	1.20	0.80	1.38	0.75
Difference between the mean Cd concentration within the upper and lower quartile ranges		0.87	0.58	1.03	0.51

5.4.2.1.2 Prediction of plant tissue Cd concentration based on soil total Cd, pH and total C

For individual plant species, backwards regression analysis was undertaken to explore wider relationships between tissue Cd concentration and the independent variables soil total Cd concentration, soil pH and soil total C (Table 5.5).

Table 5.5. Relationships between plant tissue Cd concentration and the independent variables soil total Cd, pH and total C as determined using stepwise regression with backwards elimination.

Plant species	Independent variable:			Regression equation (Plant tissue Cd =)	R^2
	Total Cd (tCd)	pH	Total C (tC)		
Chicory	****	***	***	1.828[tCd]-1.391[pH]-0.054[tC]+8.729	0.745
Plantain	**	*	n.s.	0.642[tCd]-0.681[pH]+4.258	0.290
Ryegrass	**	n.s.	n.s.	0.062[tCd]+0.059	0.230
White clover	n.s.	n.s.	n.s.	n.a.	n.a.

*P≤0.1 **P≤0.05 ***P≤0.01 ****P≤0.001 n.s. = not significant n.a. = not applicable

The combination of soil total Cd, pH and total C could not satisfactorily account for the variation in white clover tissue Cd concentration (Table 5.5). Furthermore, neither soil pH nor total C was able to improve the prediction of ryegrass tissue Cd concentration beyond the significant ($P < 0.05$) positive correlation to soil total Cd (Table 5.5). For plantain, in addition to the significant ($P < 0.05$) positive correlation between plant tissue Cd concentration and soil

total Cd concentration, a significant ($P < 0.1$) negative correlation between tissue Cd concentration and soil pH was also apparent. However, the overall coefficient of determination for plantain was still poor ($R^2 = 0.290$; Table 5.5).

Chicory was the only plant species for which the ability to predict tissue Cd concentration markedly improved through the inclusion of soil pH and total C as additional regression variables, with the coefficient of determination (R^2) increasing from 0.55 for soil total Cd alone (Figure 5.3.a), to 0.75 for total Cd, pH and total C (Table 5.5). Tissue Cd concentration in chicory proved to be significantly ($P <0.001$) positively correlated to soil total Cd, and significantly ($P <0.01$) negatively correlated to both soil pH and total C.

As the importance of soil pH and organic matter content in influencing soil Cd phytoavailability is widely recognised in the literature (McBride, 1989; McBride *et al.*, 1997; Christensen and Haung, 1999; Gray *et al.*, 1999d; Loganathan *et al.*, 2012) it is surprising that these two variables bore little relationship to Cd accumulation in plantain, ryegrass and white clover. The lack of a strong relationship for ryegrass and white clover may be a result of the relatively narrow range in tissue Cd concentrations, in addition to the possibility of inter-cultivar variation, which is known to drive wide variation in tissue Cd accumulation within a species (Florijn and Van Beusichem, 1993; McLaughlin *et al.*, 1994b; McLaughlin *et al.*, 1997; Gray *et al.*, 2001; Dunbar *et al.*, 2003; Gray and McLaren, 2005). However, this does not explain the weak relationship for plantain, since all samples were from the same cultivar (*Ceres Tonic*).

The 'goodness of fit' for actual versus predicted chicory tissue Cd concentrations is shown in Figure 5.4.a for predictions based on soil total Cd concentration alone (using the regression equation in Figure 5.3.a), and Figure 5.4.b for predictions based on the combination of soil total Cd, pH, and total C (using the regression equation in Table 5.5). Similar relationships were not plotted for the other plant species, due to their poor overall correlation (Table 5.5). The tighter alignment around the 1:1 line and corresponding greater coefficient of determination

in Figure 5.4.b illustrates the apparent sensitivity of this plant species to the effects of soil total C and pH on Cd phytoavailability (although overall, soil total Cd concentration is still the most dominant variable (Table 5.5)). This is exemplified by the two samples highlighted in red and yellow in Figure 5.4.a&b. The yellow marker represents a sample from a pumice soil with relatively low total Cd concentration (0.48 mg kg^{-1}), very low soil pH (5.1) and moderate total C content (5.5%). Based on soil total Cd alone, tissue Cd concentration at this survey site was under-predicted by approximately 60% (Figure 5.4.a). This deviation was approximately halved when soil pH and total C were also included as predictive variables (Figure 5.4.b).

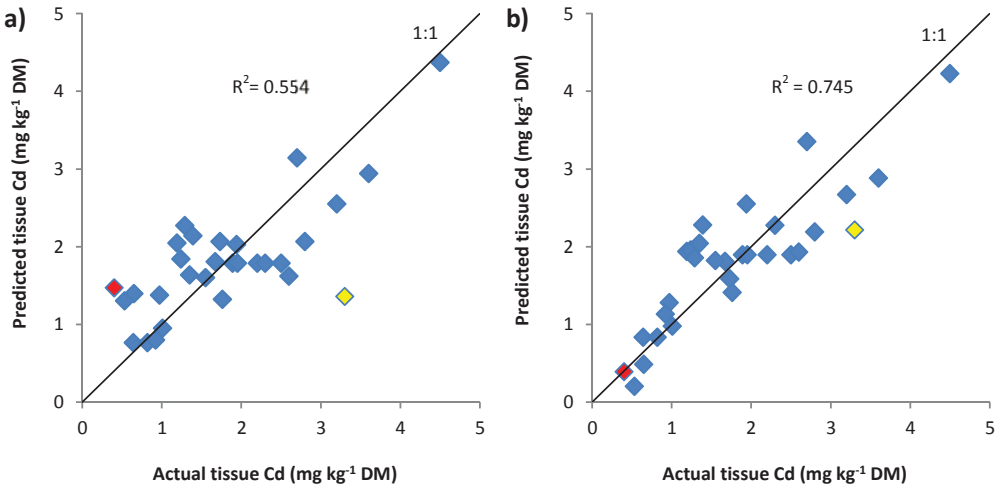

Figure 5.4. Predicted versus actual tissue Cd concentrations for chicory, based on **a)** soil total Cd (*Tissue Cd = 1.860[Soil total Cd] + 0.467),* and **b)** soil total Cd, pH and total C (*Tissue Cd = 1.828[Soil total Cd] - 1.391[Soil pH] - 0.054[Soil total C] + 8.729*).

In the second example, the red marker represents a tissue sample from an Organic soil with a relatively low total Cd concentration (0.54 mg kg^{-1}), moderate soil pH (5.5) and very high total C content (31%). In this case, the tissue Cd concentration predicted on soil total Cd concentration alone was over three times greater than the measured tissue Cd concentration (Figure 5.4.a). However, predicted and measured tissue Cd concentrations were very closely aligned when soil pH and total C were also taken into account (Figure 5.4.b). Furthermore, despite the similar soil total Cd concentrations for the yellow and red marked chicory samples

(0.48 and 0.54 mg kg^{-1}, respectively) the difference in tissue Cd concentration between these two samples (2.9 mg kg^{-1} DM) further illustrates the importance of including soil total C and pH to improve prediction of tissue Cd accumulation in this plant species.

Notably, Gray *et al.* (1999d) developed an algorithm (Equation 1) based on soil total Cd, organic matter and soil pH, which explained 76% of the variability in soluble Cd concentrations across 29 New Zealand soils:

$$Log[Cd]_S = 7.28 - 0.89pH + 1.21LogCd_T - 1.04LogOM \quad (1)$$

where *Log* refers to base-10 logarithms for Cd_S (Cd concentration in soil solution, µg L^{-1}), Cd_T (soil total Cd concentration, mg kg^{-1}) and *OM* (soil organic matter, g kg^{-1}).

By converting the total C values of this study to organic matter using the Van Bremmelen factor of 1.724 (Tan, 2005) the relationship between chicory tissue Cd concentration and the predicted Cd concentration in soil solution can be developed for the field survey dataset. Figure 5.5 shows that the Cd solubility model of Gray *et al.* (1999d) was able to successfully predict chicory tissue Cd concentration. Using log-transformed data for consistency, the significance and coefficient of determination ($P < 0.001$, $R^2 = 0.764$; Figure 5.5.a) is similar to the upper end of the range ($P = 0.05$-<0.001, $R^2 = 0.41$-0.83) reported for various plant species by Gray *et al.* (1999a). The research presented by these authors indicated that the predictive model was most robust ($P < 0.001$, $R^2 = 0.77$-0.83) for species containing greater tissue Cd concentration ranges (i.e. carrot and lettuce). These species contained Cd concentration ranges comparable to that for chicory within this field survey.

Log-transforming data reduces variance in the predictive relationship as soluble Cd concentration increases, as shown by the difference in the linear regressions using log-transformed soluble Cd and chicory Cd data ($R^2 = 0.764$; Figure 5.5.a) versus back-transformed soluble Cd and chicory Cd data ($R^2 = 0.616$; Figure 5.5.b). However, the regression on back-transformed data can be directly contrasted against the linear regression performed on the

raw, unlogged data in this study (Table 5.5). This indicates that the model developed in this study on the variables soil total Cd, pH and total C, gives a more robust prediction of chicory Cd concentration (R^2 = 0.745) than the Cd solubility model of Gray *et al.* (1999d).

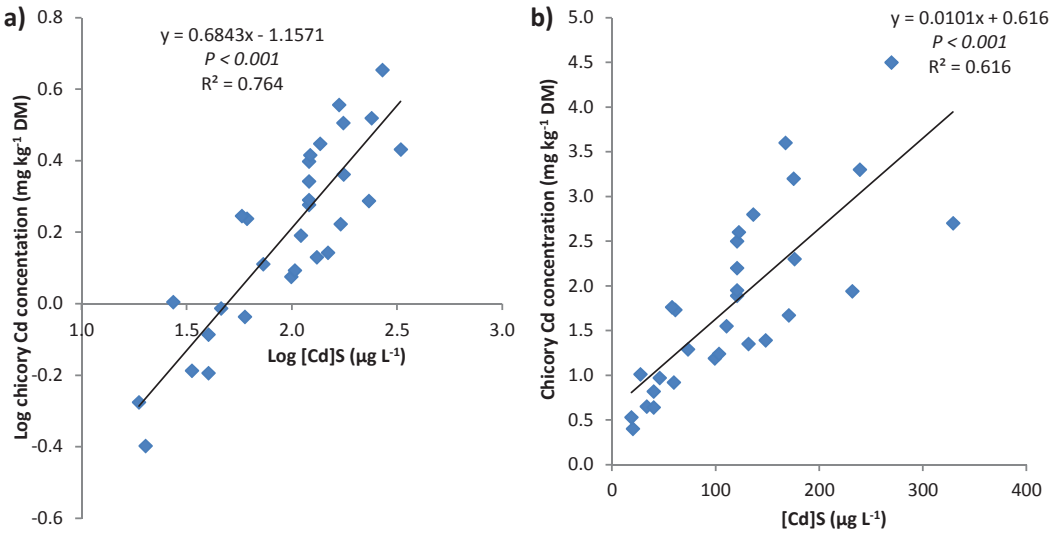

Figure 5.5. Relationship between soluble Cd concentration ([Cd]S) (Gray *et al.*, 1999d) and chicory Cd concentration across the field survey sites; **a)** log-transformed (for consistency with Gray *et al.* (1999a)), and **b)** back-transformed from logarithmic data.

The reason for the better prediction of chicory Cd concentration for the model developed from this field survey (Table 5.5) may be related to the much greater range in soil total Cd concentrations in the soils of the field survey (0.16-2.10 mg kg^{-1}) than in the Cd solubility research (0.03-1.34 mg kg^{-1}) of Gray *et al.* (1999d). Unlike soil total Cd, soil pH and total C ranges for chicory sites within the current field survey (pH = 5.0-6.6, total C = 2.2-38.2%) were similar to those within the soils used in the Cd solubility research (pH = 4.8-6.2, total C = 2.4-34.3%) of Gray *et al.* (1999d). Another possible factor is that 60% of the sites from the field survey that were used to derive the relationship between soil total Cd, total C, pH and chicory tissue Cd concentration represented a single soil order (Allophanic). Clay mineralogy was not included as a regression variable, but it is possible that having a large proportion of soils with similar mineralogy (and therefore Cd sorption and solubility characteristics) could reduce

overall variability in the dataset. In contrast, the 29 soils used by Gray *et al.* (1999d) had no such soil order bias.

5.5 Conclusions

The findings from this field survey validate the results obtained in a previous glasshouse trial (Chapter 4; Stafford *et al.* (2016)) where tissue Cd concentration was found to be significantly enriched in chicory and plantain relative to ryegrass and white clover. The wide range in tissue Cd concentrations for chicory (0.40-4.50 mg kg^{-1} DM) and plantain (0.23-2.40 mg kg^{-1} DM) observed in this survey reflects the sensitivity of these plant species to changes in soil Cd phytoavailability, although only the variation in tissue Cd concentration for chicory was able to be satisfactorily explained (R^2 = 0.745) by the soil factors total Cd, pH and total C. The low tissue Cd concentrations for ryegrass or white clover and weak to non-existent relationship with soil total Cd, pH and total C reinforces that animal Cd accumulation risk is minimal when grazing these forages, even under Cd-enriched soil conditions. The ability to predict chicory tissue Cd concentrations from soil total Cd concentration, pH and total C could be useful for guiding land management decisions for sowing chicory. As previous modelling (Chapter 4; Stafford *et al.* (2016)) has suggested increased livestock kidney Cd accumulation risk when grazing high Cd forages, animal grazing trials are recommended to evaluate Cd partitioning in grazing ruminants when grazing Cd-enriched chicory / plantain crops.

CHAPTER 6 : Prediction of total carbon, nitrogen and cadmium concentrations with soil depth using visible and near-infrared reflectance spectroscopy

6.1 Abstract

In this study, visible and near-infrared reflectance spectroscopy (NIRS) was used to predict variation in soil total carbon (C), total nitrogen (N) and total cadmium (Cd) concentrations with soil depth. Soil cores were collected intact to 400-600 mm depth from two long-term dairy farms with contrasting soils, P fertiliser and land management history. Specific to each property, partial least squares regression (PLSR) was undertaken to calibrate spectral reflectance data against total C and total N measured within 50 mm soil core depth increments. The resultant predictive models were able to successfully predict soil total C (R^2 = 0.91-0.95, RMSECV(%) = 0.40-0.64, RPD = 3.41-4.33) and total N concentrations (R^2 = 0.91-0.92, RMSECV(%) = 0.04-0.08, RPD = 3.43-3.57). Based on the strong correlation between measured soil total Cd and total C / N within each property (R^2 = 0.83-0.90), regression relationships were extended to predict soil total Cd concentration from NIRS-predicted total C (NIRS-C) and/or total N (NIRS-N) concentrations. Soil profile total Cd concentrations and variation with depth was similar for measured and NIRS-C and/or NIRS-N predictions, although relationships between total Cd and soil total C / N are site specific and non-transferable. Overall, NIRS shows promise as a rapid in-field diagnostic tool, allowing low-cost paddock-specific assessment of soil total C / N concentrations. This information will be useful to understand tillage history, and consequently to interpret variation in soil total Cd concentrations between paddocks and with soil depth.

6.2 Introduction

Cadmium is a non-essential element that has been related to human health disorders (Chaney *et al.*, 1999) and soil eco-toxicity effects (McGrath, 1999). As plant uptake of Cd is related to soil Cd phytoavailability (Adriano, 1986; Smolders and Mertens, 2012) accumulation of Cd is undesirable in agricultural soils. Accumulation of Cd in New Zealand agricultural soils has been directly linked to P fertiliser application history (Bramley, 1990; Roberts *et al.*, 1994; Zanders *et al.*, 1999). As a consequence, a Tiered Fertiliser Management System (TFMS) was recently introduced to manage the risk of on-going Cd accumulation over a 100-year timeframe (MAF, 2011). This system imposes increasing limitations to P fertiliser management options (types and rates) to reduce Cd inputs as soil Cd concentrations increase, with four soil Cd concentration trigger values (0.6, 1.0, 1.4 and 1.8 mg kg^{-1}) being used to separate five Cd management tiers (Cavanagh, 2012; FANZ, 2016). Furthermore, although agricultural land use is exempt from the soil contaminant standards (SCS) that were recently introduced under the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health (NES) (MfE, 2011), application of this framework has potential to limit land use flexibility where soil Cd concentrations exceed landuse-specific SCS. For example, conversion of agricultural land to rural-residential land use requires remediation where soil Cd concentrations exceed 0.8 mg kg^{-1} (MfE, 2011). Notably, this soil Cd concentration is well within the range of soil Cd concentrations reported for New Zealand agricultural soils (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b). As a consequence of the introduction of the TFMS and NES, there is increasing interest in soil Cd, its variability within farming landscapes, and options to manage soil Cd concentrations where enrichment has occurred.

Soil organic matter is known to be an important sorption/exchange surface for Cd in soils (McBride, 1989; Bolan *et al.*, 1999b; Christensen and Haung, 1999; Loganathan *et al.*, 2012). For this reason, soil organic matter is known to be a key variable influencing Cd solubility and

phytoavailability (McBride *et al.*, 1997; Gray *et al.*, 1998, 1999d). As New Zealand pastoral soils are particularly rich in organic matter (typically 5-15% in mineral soils (McLaren and Cameron, 1996)), organic-bound Cd typically accounts for a dominant fraction of soil total Cd (Gray *et al.*, 1999b; Gray *et al.*, 2000). Although soil total Cd concentration has been shown to be poorly correlated to soil total C or total N concentration across different farming properties (Reiser *et al.*, 2014), previous work within this study (Chapter 3) has shown relatively strong correlations between soil total Cd and total C / total N concentrations within individual properties. This stronger relationship within a property is likely a consequence of large sources of variability that exist between properties (i.e. differences in P fertiliser management, tillage history, and soil characteristics) being minimised.

Due to its limited mobility, soil Cd taken up by pasture plants and recycled as dung and plant litter plus Cd deposited on the soil surface (via P fertiliser) accumulates in the organic matter rich topsoil of non-cultivated New Zealand pastoral soils, decreasing in concentration with increasing soil depth (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999). Variation in soil Cd concentration with depth is an important factor to consider with regard to potential management options to decrease Cd phytoavailability (e.g. tillage depth). Recent development in the use of visible and near- infrared reflectance spectroscopy (hereafter referred to simply as 'NIRS') has shown great promise for rapid and non-destructive assessment of variation in soil total C and total N concentrations (Kusumo *et al.*, 2008; Kusumo, 2009; Kusumo *et al.*, 2011). This technology may open new opportunities for more rapid and cost effective assessment of variation in soil C, N and Cd with depth, providing greater resolution in soil Cd distribution in the soil profile than is practically possible using conventional soil core analysis. The research in this chapter was undertaken to explore the use of the NIRS technique to provide greater resolution of variation in soil total C / N concentrations with soil depth, which may be used to explain spatial variation in topsoil Cd

concentrations linked to soil tillage history, and also to predict variation in soil total Cd concentrations within the soil profile.

6.3 Methodology

Sampling locations and sampling technique for the collection of intact soil cores has been described previously (Chapter 3, Section 3.4.2). Soil cores representing the Waimairi peaty loam soils of the Canterbury property were excluded from the analysis since these naturally contained much greater soil total C and total N concentrations than the predominant mineral soils found within the property. Including these atypical peaty loam soils would have introduced large prediction error to the calibration models for the mineral soils.

6.3.1 Soil core analysis

6.3.1.1 NIRS assessment of intact cores for soil total carbon and nitrogen

To provide a high resolution assessment of the variability in soil total C and total N with soil depth, the curved vertical wall of each intact soil core was scanned with an adapted FieldSpecPro spectroradiometer (Analytical Spectral Devices, Boulder, Colorado, USA). This process and associated statistical analysis was carried out by Dr. B.H. Kusumo, following the methodology detailed in Kusumo (2009). Spectral reflectance data was collected within the visible and near-infrared wavelength range of 350-2500 ηm. Data was collected in 10 mm increments along the length of each soil core, for a depth range of 0-350 mm and 0-400 mm for the Waikato and Canterbury properties, respectively. Each soil core was scanned five times. Following the methodology of Kusumo *et al.* (2008), partial least-squares regression (PLSR) analysis with leave-one-out cross validation was performed to develop a model to predict total C and total N values (NIRS-C and NIRS-N, respectively) for each 50 mm soil core section, by referencing laboratory total C and total N (Lab-C and Lab-N, respectively) data against the average NIRS spectra within each 50 mm soil core section. The calibrated NIRS-C and NIRS-N

spectral models were then used to predict soil total C and total N values from the average spectral data for each 10 mm depth increment of the intact soil cores.

6.3.1.2 Elemental analysis of intact soil core subsections

Post NIRS analysis, intact soil cores were sectioned into 50 mm depth increments in preparation for elemental analysis for total Cd, C and N. All 50 mm core sections were air-dried over several weeks in a sample drying and storage facility (approximate temperature 25 °C) before being oven-dried at 38°C for a minimum of 16 hours, and then crushed to pass through a 2 mm sieve. Analytical methodology for total Cd, total C and total N for the intact soil core subsections was detailed previously in Chapter 3 (Section 3.4.4.1 and 3.4.4.3).

Comparison of measured versus NIRS-predicted variation in total C, total N and total Cd concentrations with soil depth was undertaken for two sites from each of the Waikato and Canterbury properties. Within the Waikato farm, site 10 Ke(A) represents an undisturbed Kereone (Allophanic) soil, while site 2 T(A) represents an undisturbed Topehaehae (Gley) soil. Within the Canterbury farm, site 30 Tm1 represents a Temuka (Gley) soil that has not undergone tillage since the early 1980's, whereas site 13 Tm2 represents a Temuka soil that was much more recently tilled (spring 2004).

6.3.2 Statistical analysis

ParLeS (Viscarra Rossel, 2008) was used to develop the PLSR models for the prediction of total C and total N concentrations from NIRS data. Following the methodology of Kusumo *et al.* (2011), the correlation strength between predicted and measured values was assessed using the following indicators; coefficient of determination (R^2), root mean square error of cross validation (RMSECV) and ratio of prediction deviation (RPD).

SPSS (IBM Corp, 2013) was used to carry out linear regression analysis to describe the relationship between measured soil total Cd and total C or total N concentrations for individual

50 mm soil core sections. Stepwise regression analysis was undertaken to determine best-fit predictive models for soil total Cd based on NIRS-predicted total C and/or total N.

6.4 Results and discussion

6.4.1 Relationships between soil total Cd and total C or total N from laboratory analysis of intact soil core sections

The variation in soil total C, total N and total Cd concentrations within each property from laboratory analysis of all intact soil core 50 mm soil depth increments used in NIRS analysis is described in Table 6.1. With the Waimairi peaty loam soils excluded from the Canterbury farm dataset, the mean total C, total N and total Cd concentrations, as well as the variation about these mean concentrations, is greater for the Waikato than the Canterbury property.

Table 6.1. Variation in total C (%), total N (%) and total Cd (mg kg^{-1}) within all 50 mm soil depth increments at the Waikato and Canterbury sites as determined through laboratory analysis.

Parameter	Waikato (*n* = 172)			Canterbury (*n* = 168)		
	Total C	Total N	Total Cd	Total C	Total N	Total Cd
Min	0.33	0.05	0.01	0.23	0.04	0.02
Max	11.10	1.17	1.55	6.36	0.59	0.47
Median	2.24	0.27	0.35	1.86	0.20	0.12
Mean	3.41	0.37	0.48	2.05	0.22	0.15
Variance	7.66	0.08	0.17	1.81	0.02	0.01

Within each property, linear regression analysis using all individual 50 mm soil core sections revealed that total C and total N were both significantly ($P < 0.001$) related to soil total Cd, and accounted for a large proportion (83-90%) of the variability in soil total Cd concentrations (Table 6.2). The coefficient of determination was similar for total N and total C for both the Waikato (R^2 = 0.90 versus 0.87, respectively) and Canterbury (R^2 = 0.87 versus 0.83, respectively) properties.

Table 6.2. Relationship between soil total Cd (mg kg^{-1}) and total C (%) or total N (%) from linear regression analysis across all 50 mm soil core sections.

Property	Prediction variable	*P* value	R^2
Waikato	Lab-C	*<0.001*	0.87
	Lab-N	*<0.001*	0.90
Canterbury	Lab-C	*<0.001*	0.83
	Lab-N	*<0.001*	0.87

6.4.2 Relationship between measured and NIRS-predicted soil total C and total N

Correlation data for the PLSR relationship between NIRS-predicted and measured soil total C and total N concentrations for 50 mm soil core sections is provided in Table 6.3. Based on the criteria for NIRS calibration performance of Malley *et al.* (2004), the spectral models were able to 'successfully' predict soil total C and total N concentrations for both properties (R^2 = 0.90-0.95, RPD = 3-4). The correlation strength was stronger than that previously reported for NIRS analysis of intact soil cores by Kusumo *et al.* (2008) (total C: R^2 = 0.75, RMSEP = 1.21%, RPD = 2.01; total N: R^2 = 0.86, RMSEP = 0.07%, RPD = 2.66) and Kusumo *et al.* (2011) (total C: R^2 = 0.86, RMSECV = 0.48%, RPD = 2.66; total N: R^2 = 0.81, RMSECV = 0.05%, RPD = 2.32). In those two studies, NIRS assessment methodology differed in that spectral scans were taken incrementally at specified depths using the flat horizontal surface area of sectioned soil cores, rather than scanning continuously along the curved vertical wall of the entire soil core. As reported by Kusumo (2009), the flat horizontal surface NIRS analysis approach provides less robust assessment of soil total C and total N concentrations than the vertical wall approach, since it only provides point-analysis at a limited number of depths within the soil profile.

Table 6.3. Relationship between measured (Lab) and predicted (NIRS) soil total C (%) and total N (%) for 50 mm soil core sections.

Farm	Parameter	Regression equation	R^2	RMSECV(%)	RPD
Waikato	Total C	NIRS-C = 0.9499(Lab-C) + 0.1661	0.95	0.64	4.33
	Total N	NIRS-N = 0.9289(Lab-N) + 0.0264	0.91	0.08	3.43
Canterbury	Total C	NIRS-C = 0.9402(Lab-C) + 0.1248	0.91	0.40	3.41
	Total N	NIRS-N = 0.9445(Lab-N) + 0.0123	0.92	0.04	3.57

Measured (50 mm depth increments) versus NIRS-predicted (10 mm depth increments) total C and total N with depth are provided for two sites each from the Waikato (Figure 6.1) and Canterbury (Figure 6.2) properties. At all four sites, NIRS-predicted and measured soil total C and total N concentrations show very similar patterns with depth for both sites, reflecting the strong PLSR correlations shown in Table 6.3. Overall, the tight relationship between measured

and NIRS-predicted total C / N as shown in Figure 6.1 and Figure 6.2, and described in Table 6.3 agrees with previous findings using the same technique to predict soil total C and N concentrations (Kusumo, 2009).

Both the Kereone (10 Ke(A)) and Topehaehae (2 T(A)) soils within the Waikato farm show a consistent decline in total C and N with depth (Figure 6.1) that is expected under undisturbed, non-cultivated pastoral conditions (Kelliher *et al.*, 2012) that were present within that property. Within the Canterbury property, a similar decline in soil total C / N concentration with increasing depth is also seen at site 30 Tm1. In contrast however, soil total C and total N concentrations were relatively uniform to approximately 200 mm depth at site 13 Tm2 (Figure 6.2). The contrasting soil total C / N profiles within the Canterbury site reflect differences in soil tillage history. Site 30 Tm1 has not been tilled for 30-35 years as a consequence of this paddock being routinely used for harvesting silage during the 1980's and 1990's. In contrast, the paddock represented by site 13 Tm2 was mouldboard ploughed (200 mm depth) and cultivated in 2004. The relatively consistent total C / N concentrations within the 0-200 mm soil layer reflect the redistribution and homogenisation of soil organic matter that occurs with ploughing and cultivation (Sun *et al.*, 2011; Kahle *et al.*, 2013).

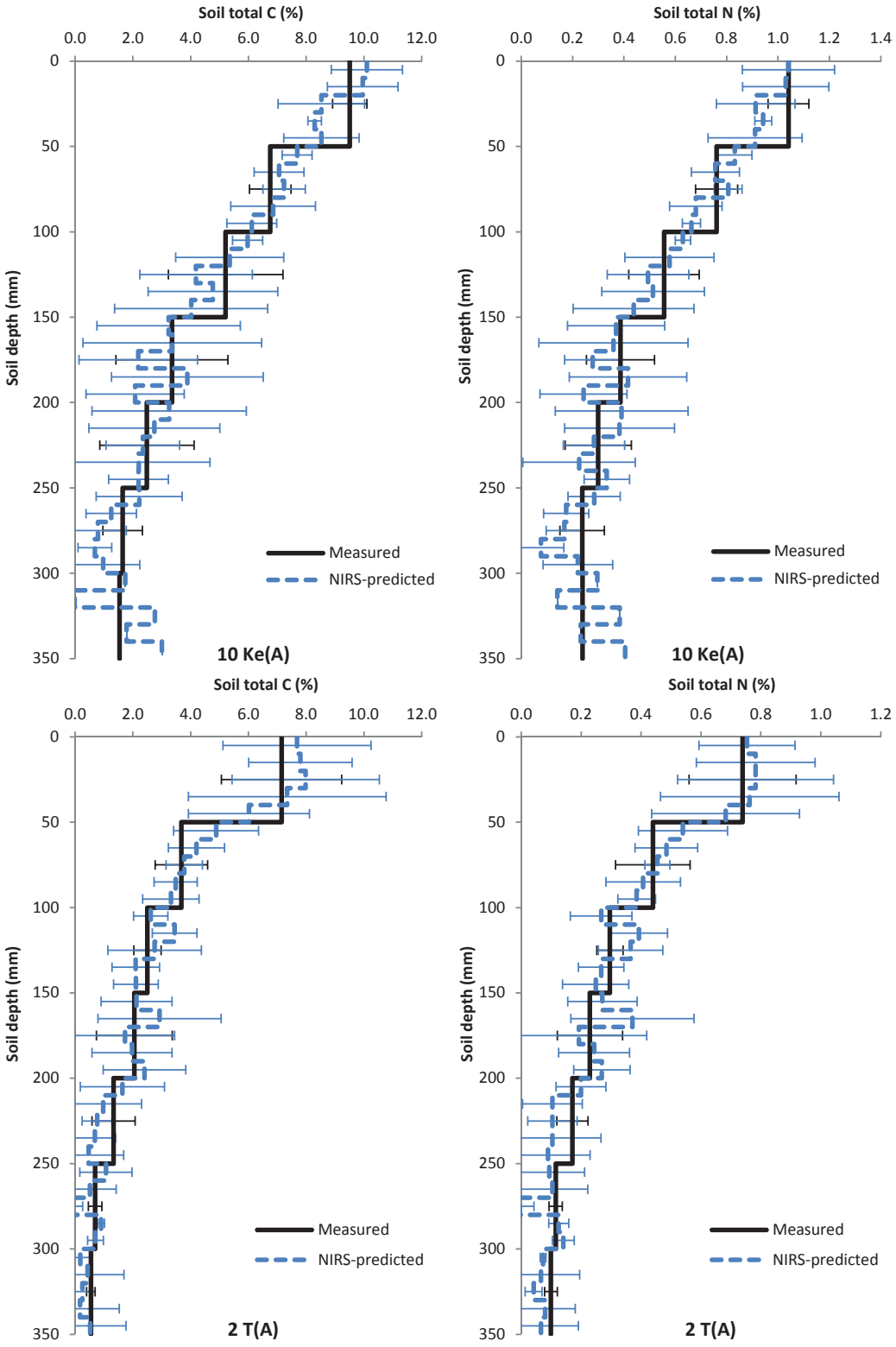

Figure 6.1. Comparison of measured (50 mm depth increments) versus NIRS predicted (10 mm depth increments) total C and total N concentrations with depth, for sites 10 Ke(A) and 2 T(A) at the Waikato property. Error bars represent the standard deviation.

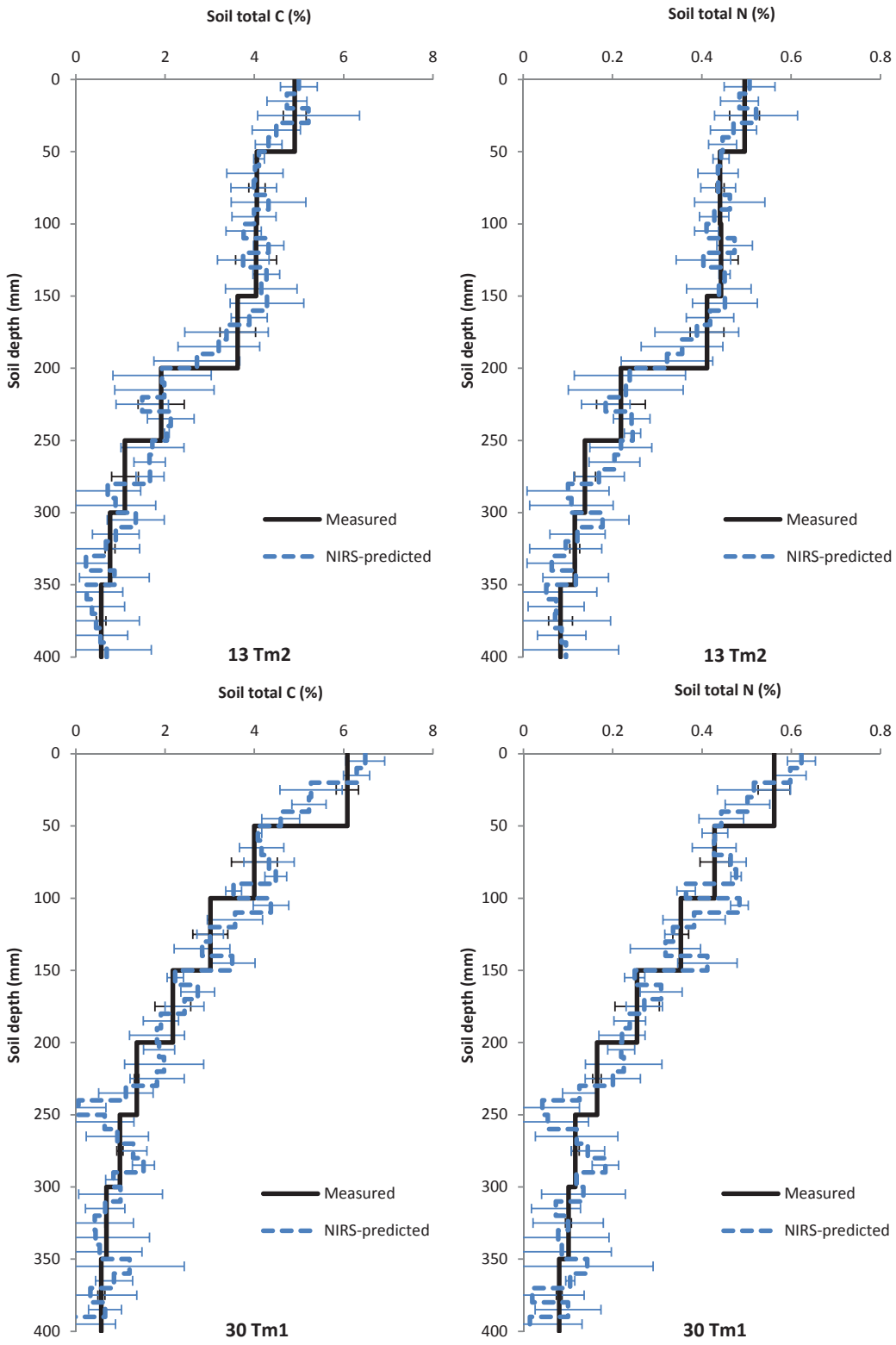

Figure 6.2. Comparison of measured (50 mm depth increments) versus NIRS predicted (10 mm depth increments) total C and total N concentrations with depth, for sites 13 Tm2 and 30 Tm1 at the Canterbury property. Error bars represent the standard deviation.

6.4.3 Prediction of soil total Cd using NIRS-predicted soil total C and total N

Relationships between measured soil total Cd and mean NIRS-predicted N and/or C for 50 mm depth increments of intact soil cores of both properties are shown in Table 6.4. For the Waikato property, stepwise regression analysis indicated that there was a significant (P < 0.001) relationship between soil total Cd concentration and NIRS-N. NIRS-C did not further improve the prediction of total Cd (P = 0.122) and was excluded from the predictive algorithm. Both NIRS-N and NIRS-C were included as significantly (P < 0.001 and P = 0.008, respectively) correlated prediction variables for soil total Cd concentration in soil cores of the Canterbury property. The coefficient of determination for the 'best-fit' total Cd predictive models was similar for both the Waikato and Canterbury properties (R^2 = 0.829 and 0.821, respectively); only slightly weaker than those determined using Lab-N or Lab-C (Table 6.3).

Table 6.4. Best fit relationship between measured soil total Cd (Lab-Cd (mg kg^{-1})) and NIRS predicted total C (NIRS-C (%)) and/or total N (NIRS-N (%)) for 50 mm soil core sections, determined using stepwise regression analysis.

Farm	Independent variable		Regression equation	*P* value	R^2
	NIRS-C	NIRS-N			
Waikato	0.122	<0.001	Lab-Cd = 1.395(NIRS-N) - 0.038	*<0.001*	0.829
Canterbury	0.008	<0.001	Lab-Cd = 1.376(NIRS-N) - 0.060(NIRS-C) - 0.034	*<0.001*	0.821

6.4.4 Soil total Cd with depth – measured versus NIRS-predicted

Using the NIRS-N / NIRS-C regression relationships with total Cd as shown in Table 6.4, soil total Cd concentration was predicted in 10 mm soil depth increments. NIRS-predicted soil total Cd concentrations were then plotted against those measured in the laboratory for each 50 mm soil depth increments. Figure 6.3 shows this data for the four sites that were previously used to illustrate measured versus NIRS-predicted soil total C/N soil profiles; sites 10 Ke(A) and 2 T(A) at the Waikato farm, and sites 13 Tm2 and 30 Tm1 at the Canterbury farm.

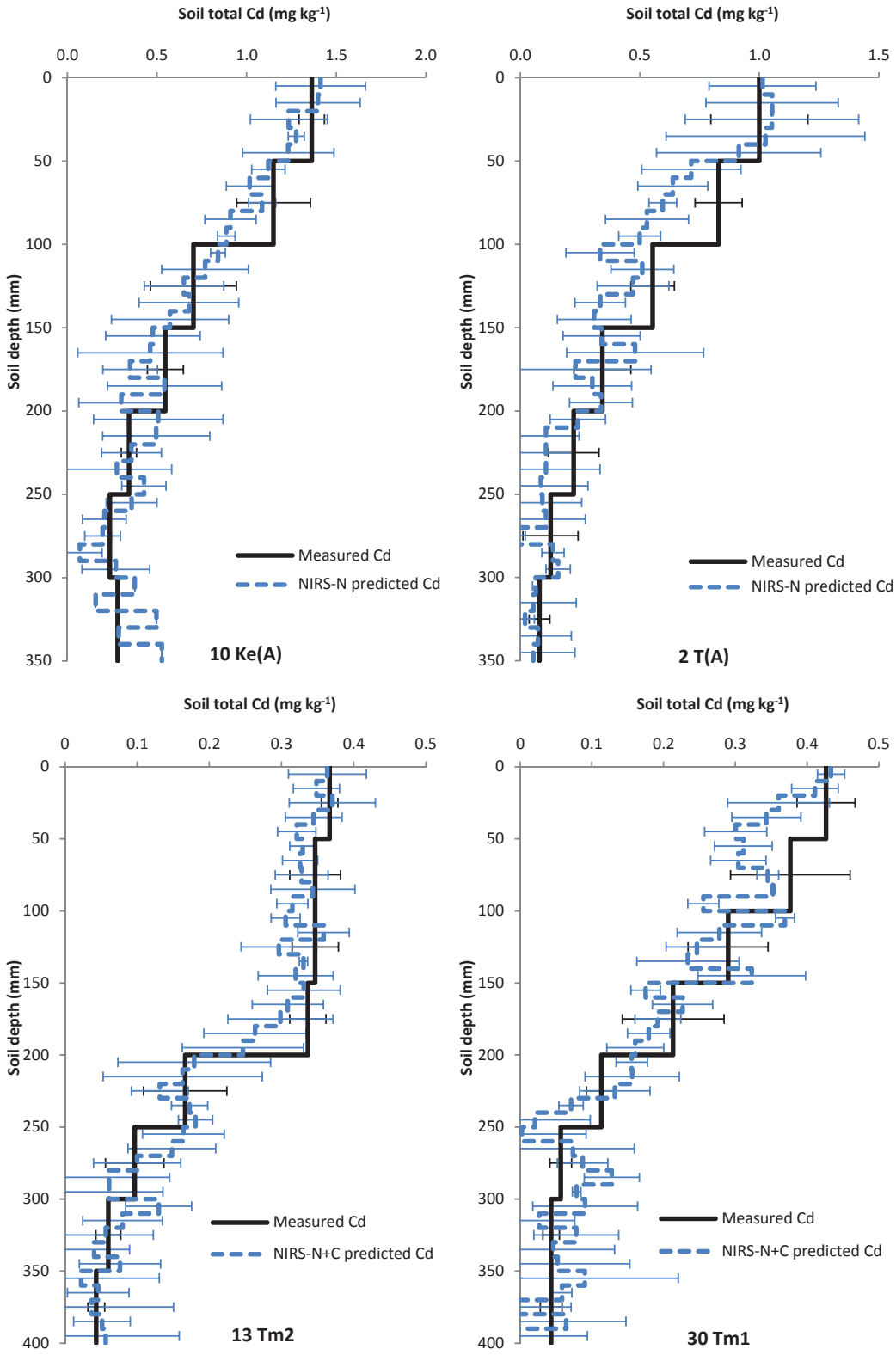

Figure 6.3. Comparison of measured (50 mm depth increments) versus NIRS-predicted (10 mm depth increments) total Cd with depth for sites 10 Ke(A) and 2 T(A) within the Waikato property, and 13 Tm2 and 30 Tm1 within the Canterbury property. Error bars represent the standard deviation.

Although there was large variation around mean-measured and mean-predicted soil Cd concentrations, absolute soil total Cd concentrations and relative change with increasing soil depth predicted from NIRS-N (Waikato) and the combination of NIRS-N and NIRS-C (Canterbury) were very similar to those measured. At both sites evaluated within the Waikato farm (10 Ke(A) and 2 T(A)) and at site 30 Tm1 within the Canterbury farm, predicted and measured soil Cd concentrations steadily decreased with increasing soil depth (Figure 6.3) consistent with soil Cd profiles from undisturbed permanent pastoral sites previously reported in the literature (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999). In contrast, in the recently tilled site within the Canterbury farm (13 Tm2) both measured and predicted soil Cd concentrations showed relatively uniform soil Cd concentrations to a depth of 200 mm, beyond which soil Cd concentrations decreased abruptly (Figure 6.3). Again, homogenisation of soil Cd concentrations within the depth of cultivation is a known consequence of intensive soil tillage (Roberts *et al.*, 1995; Chen *et al.*, 2009).

6.4.5 Application of NIRS technology for soil Cd assessment

The commercial adoption of NIRS technology for rapid, low cost analysis of C and N concentrations in agricultural soil and plant samples is now widespread (Malley *et al.*, 2004). Although largely confined to application in controlled laboratory environments with well processed samples, this study reinforces earlier research that indicated this technology has potential for in situ, rapid soil core analysis (Kusumo, 2009; Kusumo *et al.*, 2011).

This study shows that NIRS technology has two potential applications with regard to informing property-specific Cd management decisions. Firstly, the strong correlation between measured and NIRS predicted soil total C and N concentrations suggests that this approach can be useful for assessing soil tillage history. This is illustrated by the difference in soil total C / N profiles detected by NIRS analysis for site 13 Tm2 (ploughed and cultivated 10 years prior to sampling) versus 30 Tm1 (no tillage within the last 30-35 years) within the Canterbury farm (Figure 6.2)

and also the undisturbed soils of the Waikato farm (Figure 6.1). In a practical sense, paddock-specific soil Cd reconnaissance sampling could be undertaken in unison with in-situ soil core NIRS analysis for total C and N. Assessment of paddock-specific soil tillage history (defined by soil profile C/N concentration distribution) could be used to explain and interpret intra-paddock variation in topsoil Cd concentrations.

Secondly, the strong correlation between soil total C / N and total Cd concentrations within each individual property indicates that NIRS C / N assessment could be useful for evaluating variation in soil Cd concentrations with depth. However, the relationship between soil Cd concentration and soil total C / N concentration will be property-specific and non-transferable, due to differences in P fertiliser management history (and therefore Cd inputs) and soil characteristics between properties. Potentially, it could be possible to establish property-specific relationships between measured total Cd and NIRS predicted C/N within the specified soil depth range used for Cd sampling (e.g. 0-150 mm). This property-specific baseline calibration could then be used to extrapolate soil total Cd concentrations across the entire intact soil core depth range.

The distribution of soil Cd concentrations in the soil profile will be very important information in the scenario where soil Cd enrichment has result in topsoil Cd concentrations exceeding critical management thresholds. In particular, this is a very relevant issue for traditionally intensively farmed land (e.g. dairying and horticulture) on Allophanic, Pumice and Organic soil orders that are common in the Waikato, Taranaki and Bay of Plenty regions (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b; Abraham *et al.*, 2016). For example, data presented by Abraham *et al.* (2016) indicated that ten territorial authorities (mainly in the Waikato and Taranaki regions) had more than 20% of sampled farms with soil Cd concentrations greater than 1.0 mg kg^{-1}, while four of these had 5-16% of sampled farms greater than 1.4 mg kg^{-1}. Under the TFMS, farmers may wish to decrease soil Cd concentrations to allow greater flexibility in P fertiliser options (Cavanagh, 2012). Furthermore,

remediation of such Cd-enriched soils may be required to permit conversion to an alternative land use where this is desired (e.g. to meet the SCS for rural-residential land use of 0.8 mg kg^{-1} (MfE, 2011)). Soil tillage is likely to be the most practical solution to bury / dilute Cd-enriched topsoils (Roberts *et al.*, 1994, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999; Chen *et al.*, 2009). Therefore, rapid, low cost assessment techniques such as NIRS will be highly valuable to land owners, to allow site-specific determination of the required tillage depth to meet target soil Cd concentratons.

6.5 Conclusions

NIRS technology has considerable potential for rapid, in situ assessment of total C / N distribution in the soil profile. This information can provide valuable insight into paddock-specific tillage history, and consequently, the relative distribution of Cd in the soil profile. By identifying site-specific relationships between soil total Cd and total N / C, absolute soil Cd concentrations with depth can also be predicted. Where soil total Cd exceeds a designated concentration that affects land use or management (e.g. pertaining to land use flexibility under the NES) NIRS could therefore provide a useful basis for establishing the depth of inversion-tillage that is required to ensure topsoil Cd concentrations are reduced to below the designated ‘critical’ Cd concentration boundary.

CHAPTER 7 : Influence of soil moisture status on soil cadmium phytoavailability and accumulation in plantain (*Plantago lanceolata*)

This chapter was summarised in an oral presentation at the 2017 Fertiliser and Lime Research Centre conference. Citation:

Stafford, A., Jeyakumar, J., Anderson, C., Hedley, M., 2017. Influence of fluctuating soil moisture on cadmium phytoavailability and accumulation in plantain. In: Science and policy: nutrient management challenges for the next generation. (Eds L.D. Currie and M.J. Hedley). http://flrc.massey.ac.nz/publications.html. Occasional Report No. 30. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 8 pages.

7.1 Abstract

The effect of fluctuating soil moisture cycles on soil cadmium (Cd) phytoavailability was investigated in a pot trial with two contrasting soils (Kereone [Allophanic], total Cd 0.79 mg kg^{-1}; and Topehaehae [Gley], total Cd 0.61 mg kg^{-1}) that were either sown with plantain (*Plantago lanceolata*) or left unseeded. Varying soil moisture contents were established using contrasting irrigation regimes: 'flooded' (3 days flooded and then 11 days drained); or 'non-flooded' (irrigation to 70% of potted field capacity every 7 days with continuous drainage). Overall, there was no significant difference in mean 0.05 M $CaCl_2$ soil extractable Cd concentrations or plant tissue Cd concentrations between flooded and non-flooded irrigation. However, there was a consistent trend for an increase in soil extractable Cd concentrations following irrigation, regardless of the irrigation regime. Mean soil extractable Cd and plant tissue Cd concentrations were significant greater (approximately 325% and 183%, respectively) for the Topehaehae soil than the Kereone soil, despite the lower soil total Cd concentration of the Topehaehae soil. These results indicate that Cd solubility is sensitive to increases in soil moisture following periods of soil drainage, but insensitive to short-term periods of soil saturation. For Cd-accumulating crops that are likely to be sensitive to increases in soil Cd phytoavailability, management options such as deep inversion-tillage, manipulation of soil pH, and controlled

irrigation (where possible) may have a role in managing increases in Cd phytoavailability related to increases in soil moisture.

7.2 Introduction

Cadmium (Cd) is a non-essential element that is readily taken up by plants. Below phytotoxic concentration, plants have little ability to regulate Cd uptake and accumulation (Adriano, 1986). Because of this, plant tissue Cd concentrations tend to increase with increasing soil Cd phytoavailability (Williams and David, 1977; Adriano, 1986).

In addition to soil total Cd concentration, many factors are known to influence soil Cd phytoavailability. These include soil pH, organic matter content, mineralogy (i.e. clay types and abundance), the concentration of other anions and cations in soil solution, and soil redox potential (Tiller *et al.*, 1984; McBride, 1989; McLaughlin *et al.*, 1996; McBride *et al.*, 1997; Loganathan *et al.*, 2012; Young, 2012). Of these factors, soil pH is thought to be the most dominant factor controlling soil Cd phytoavailability, largely due to its overriding influence on the surface charge of variable charge clays and organic matter that dictates the soils net negative charge and therefore Cd^{2+} sorption potential (McBride, 1989; Naidu *et al.*, 1994; Naidu *et al.*, 1997; Bolan *et al.*, 1999b; Christensen and Haung, 1999; Loganathan *et al.*, 2012; Young, 2012).

Many authors have shown that moisture-driven changes in soil redox potential can also have a large influence on metal solubility (Iu *et al.*, 1981; Atta *et al.*, 1996; Charlatchka and Cambier, 2000; Kashem and Singh, 2001; Hernandez-Soriano and Jimenez-Lopez, 2012). However, most research related to soil moisture-mediated changes in Cd phytoavailability has focussed on prolonged periods of soil saturation (e.g. cultivation of rice), where development of strongly-reducing soil conditions leads to a decrease in Cd solubility through the formation of insoluble Cd-sulphide complexes (de Livera *et al.*, 2011; Zhang *et al.*, 2012; Zheng *et al.*, 2013). Prolonged soil saturation is not relevant to the management of New Zealand agricultural soils,

since these systems are based on either naturally well-drained soils or soils modified with artificial-drainage systems to control soil moisture within a desired range. As a consequence, these soils are subject to fluctuating soil moisture and only temporary periods (i.e. several days) of soil saturation that occur when rainfall (and/or irrigation) exceeds the rate of soil drainage.

Little is currently known regarding the behaviour of Cd under fluctuating soil moisture conditions punctuated by only short periods of saturation. However, numerous studies have reported increases in metal solubility following soil saturation and the associated onset of weakly- to moderately-reducing soil conditions (Charlatchka and Cambier, 2000; Cornu *et al.*, 2009; Hindersmann and Mansfeldt, 2014). This phenomenon is related to reduction-oxidation processes that govern the dissolution and precipitation of manganese (Mn) and iron (Fe) hydrous oxides. Under well-drained, aerobic soil conditions, relatively insoluble Fe^{3+} and Mn^{4+} hydrous oxides prevail (McLaren and Cameron, 1996; Hindersmann and Mansfeldt, 2014) providing an important sorption surface for many metals including Cd (Kim and Fergusson, 1992; Backes *et al.*, 1995; Gray *et al.*, 1999d; Loganathan *et al.*, 2012). However, to support microbial respiration processes under saturated, anaerobic soil conditions, Mn^{4+} and Fe^{3+} act as the electron acceptor in the place of oxygen, and in doing so, become reduced to their more soluble Mn^{2+} and Fe^{2+} oxidation states (McLaren and Cameron, 1996; Hindersmann and Mansfeldt, 2014). With the consequent sequential dissolution of Mn and Fe hydrous oxides under increasingly reducing soil conditions, co-sorbed metal ions are concurrently released into soil solution, increasing metal phytoavailability. Notably, Ponnamperuma (1972) reported that reducing conditions can be established very rapidly (within a few days), suggesting that even short periods of saturation can influence the solubility and phytoavailability of metals sorbed to Fe / Mn hydrous oxides. This observation is supported by the work of Bhatti *et al.* (2013), who attributed an increase in plant tissue As concentration to the dissolution of Fe

hydrous oxides for plants grown under a cyclical 3-day flooded/11-day drained irrigation regime, relative to plants grown under continuously drained conditions.

Due to the affinity between Cd^{2+} and Fe/Mn hydrous oxides, there is potential that Cd phytoavailability could also be influenced by short-term periods of soil saturation, similar to the effects on As as shown by Bhatti *et al.* (2013). If this hypothesis is correct, differences in soil extractable Cd concentration should be detectable over time (in addition to differences in plant Cd accumulation), since these should directly relate to the contrasting soil hydrological conditions (and redox potentials) imposed. The research described in this paper was therefore undertaken to quantify the effect of fluctuating soil moisture content and short-term periods of soil saturation on soil Cd phytoavailability and plant tissue Cd accumulation. Improving our understanding of the impact of soil moisture fluctuations on soil Cd phytoavailability may provide greater insight into appropriate strategies to better manage Cd accumulation in agricultural plant species.

7.3 Methodology

The research described in this paper was conducted as a pot-trial, under controlled conditions, over the period April-September 2015. Two irrigation/soil moisture regimes were overlain on two contrasting soils (Kereone silt loam and Topehaehae sandy clay loam; Table 7.1), which were either sown in plantain (*Plantago lanceolata*, cultivar 'Ceres Tonic') or left as an unplanted control. Five replicates of each treatment were used (i.e. 40 pots in total).

Table 7.1. New Zealand Soil Classification and characteristics of the two soils used in this study.

Soil type	New Zealand Soil Classification	tCd	tP	tMn	tFe	tC	pH	CEC	P retention
		(mg kg^{-1} DW)			(%)			(meq/100 g)	(%)
Kereone silt loam	Typic Orthic Allophanic	0.79	1577	1840	2.1	5.7	6.3	26	69
Topehaehae sandy clay loam	Typic Recent Gley	0.61	1132	710	2.4	3.2	5.6	17	34

Plantain was chosen as the Cd phytoavailability indicator species in this trial based on previous research (Stafford *et al.*, 2016) which recorded high tissue Cd concentrations in this cultivar. Although chicory was shown to accumulate even greater tissue Cd concentrations than plantain (Stafford *et al.*, 2016) 'Ceres Tonic' plantain is known to have greater cool season growth rate (Powell *et al.*, 2007), an important factor given this trial was carried out over winter.

The imposed irrigation strategies (based on the methodology of Bhatti *et al.* (2013)) were (i) 'non-flooded', where soil moisture was maintained at 70% potted field capacity (Fc_P) utilising a 7-day irrigation cycle; and (ii) 'flooded', where soil moisture was maintained at 110% Fc_P for 3 days, subsequent to which drainage was permitted allowing aeration of the soil over the ensuing 11 days, before the 14-day irrigation cycle was repeated.

7.3.1 Pot design

To facilitate the proposed irrigation / soil moisture strategies, square white plastic pots (16.5 x 16.5 x 19 cm) were prepared based on the methodology of Bhatti *et al.* (2013). Briefly, for flood irrigated pots, a 7 mm diameter hole was drilled into the side of the pot approximately 2 cm above the base. Into this, a 30 cm length of rubber tube (external diameter 8 mm and internal diameter 4 mm) was inserted such that 15 cm of tube extended across the internal width of the pot and 15 cm extended externally (Figure 7.1). The section of rubber tube inside the pot had a narrow slit (12 cm x 0.3 cm) cut out along the length of the tube. This internal rubber tube was then wrapped in mulch mat to prevent potential sediment blockage or loss. To facilitate flooded soil conditions for 3 days, the external length of rubber tube was bent over itself and clamped to prevent drainage. During the subsequent 11-day drained period, the tube was unclamped to facilitate soil drainage and aeration.

Pots used for non-flooded conditions had two 3 mm diameter holes drilled into the base of each side (i.e. 8 holes per pot) to permit drainage. A 20 x 20 cm section of non-woven mulch

mat was placed in the bottom of each non-flooded treatment pot. This water-permeable fabric extended approximately 2 cm up the internal wall of each pot, preventing soil loss through or blockage of the drainage holes located near the base of each side. The bottom of all pots was then filled with 400 g of gravel (6-13 mm) to facilitate aeration and water movement around the drainage holes / tube. All pots were then weighed to determine mass without soil added.

Figure 7.1. Design of pots (left, completed; right, partially complete showing the slit in the internal drainage tube) used for generating cyclical 3-day flooded, 11-day drained soil conditions (photograph courtesy of the author).

7.3.2 Soils

Soils were collected from a commercial dairy farm in the Waikato region of New Zealand. Classification and chemical characteristics of the two soils is provided in Table 7.1. At the collection sites, the top 30 mm of soil was scraped off to remove the dense root mat of the ryegrass/white clover pasture sward. Soil from the A-horizon was then retrieved from 30-150 mm depth and sieved (field-moist) to 4 mm. Each pot was packed with 3500 g of field moist soil, with a subsample of each soil taken for moisture content determination (24 hours at 105 °C). The dry-soil gravimetric moisture content at potting was calculated at 0.42 and 0.43 for the Topehaehae and Kereone soils, respectively. On this basis, the oven-dry corrected mass of soil in each pot was 2464 and 2451 g for the Topehaehae and Kereone soils, respectively.

All pots were then watered until the soil was saturated. Once drainage had ceased, pots were re-weighed to determine the mass of water in each pot at Fc_P. This mass of water at Fc_P was then multiplied by either 70% or 110%, and added to the combined mass of the oven-dry soil and pot apparatus, so as to determine the target total pot mass for each soil type x irrigation treatment.

7.3.3 Experimental layout and management

All pots were laid out in 4 rows of 10 pots in completely randomised design. The trial was carried out under a clear Perspex-roofed shelter at ambient air temperature (ranging from 0.1 to 21.7 °C) in Tauranga, Bay of Plenty. Daily mean, minimum and maximum air temperature data for Tauranga over the experimental period is shown in Figure 7.2. Throughout the duration of the trial, pots were rotated on a weekly basis to ensure there was no environmental bias for any replicate.

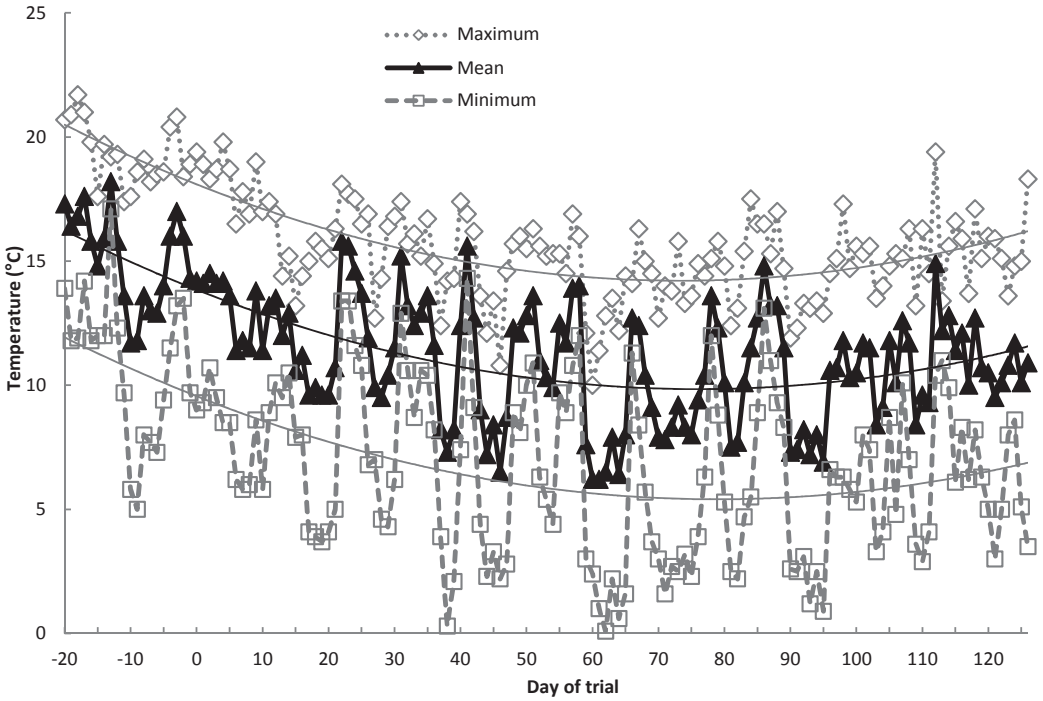

Figure 7.2. Daily mean, maximum and minimum temperatures recorded at Tauranga airport (NIWA 'CliFlo' climate station 1615) over the duration of the trial period.

Plantain seeds were sown in the appropriate pots on 20 April 2015 (day -20). Divergence in irrigation strategy occurred on 10 May 2015 (day 0), once seedlings had germinated, become well established, and had been thinned to one healthy plant per pot. The trial was completed on 13 September 2015 (day 126).

7.3.4 Soil sampling and plant harvest

Immediately prior to the initiation of the different irrigation strategies (day 0) a single soil core (100 mm depth, 18 mm diameter) was extracted from each pot. Further soil samples were taken 3 days later, timed in alignment with the end of the 3-day 'saturated' phase of the flooded treatments. Flooded treatments were allowed to drain over the subsequent 11 days, before this 'pre-irrigation' and '+3 day' sampling strategy was repeated, coinciding with each 14-day flood irrigation cycle. In total, this fortnightly soil sampling cycle was repeated 9 times (i.e. 18 paired samples). Soil removed at each sampling was backfilled with surplus soil from each soil type that had been sieved and kept in storage. Soil sampling sites were rotated clockwise around each pot, with the location of backfilled soil sampling sites marked with a toothpick.

Plantain was harvested from all pots when 'grazing-maturity' was reached within the treatments exhibiting the greatest growth rates (non-flooded Kereone and Topehaehae treatments). This occurred on day 126. Plant tissue samples were harvested 20 mm above the soil surface, weighed, washed and oven-dried (60°C for 3 days) for dry matter content (% DM), dry matter yield (g DM pot^{-1}) and tissue Cd (mg kg^{-1} DM) assessment.

7.3.5 Chemical analysis

7.3.5.1 Plant tissue Cd concentration

Plant tissue samples were dried in their paper bags at 60°C for 3 days in a forced-air convection oven. Samples were then crushed and homogenised prior to analysis for Cd, following the

methodology described by Jeyakumar *et al.* (2014) for plant metal analysis. Briefly, 0.1 g of each sample was digested in 10 mL of 69% HNO_3 for 2-3 hours at 120°C. Samples were then diluted to 50 mL with deionised water and vortex stirred, before filtering with Whatman No. 42 filter paper. Aliquots of the filtered digest solution were then analysed by Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, Perkin-Elmer AAnalyst 600). Within each batch run of approximately 60 digestion samples, a standard reference material (NIST 1573a [National Institute of Standards and Technology; tomato leaves]) and method blanks (acid-only) were also included. These were run as a check on analytical accuracy every 10 samples, with the analysed concentration differing by less than 5% of the certified value. GFAAS calibration rescale was performed every 30 samples. The instrument limit of detection (LOD) for Cd using the GFAAS is 0.002 mg L^{-1} (Dr P. Jeyakumar, personal communication, August 17, 2015).

7.3.5.2 Soil extractable Cd concentration

Following the procedure of Li *et al.* (2001) 6 g of field moist soil was extracted in 30 mL of 0.05 M $CaCl_2$ with 24 hours end-over-end shaking. The samples were then centrifuged at 11,953 g for 10 min before filtering (Whatman No. 42). Aliquots of filtrate was then analysed for Cd via GFAAS, following the procedure described in previously. Results were corrected to an oven-dry soil-equivalent post-analysis. The pH of 0.05 M $CaCl_2$ soil extracts was assessed for all samples at sampling days 0, 28, 84 and 112. This was undertaken using an Eutech Instruments CyberScan pH 310 fitted with an Ag/AgCl oxidation reduction potential reference electrode.

7.3.6 Quality control

All chemicals used in the experiments were of analytical grade. The GFAAS limit of detection for Cd in digest solution was 0.002 mg L^{-1}. Analytical accuracy was assessed through parallel analysis of a certified standard reference material (NIST 1573a, tomato leaves). GFAAS calibration rescale was performed every 30 samples.

7.3.7 Statistical analysis

Statistical analysis was carried out using the software SPSS (IBM Corp, 2013). Significant outliers were identified using Tukeys outlier filtering method (Tukey, 1977). Analysis of variance (ANOVA) was undertaken to assess for differences in treatment means, and Tukeys honestly significant difference (HSD) was run as a post-hoc analysis to identify differences between individual treatment means.

7.4 Results

7.4.1 Soil extractable Cd concentration

The mean soil extractable Cd concentration across the duration of the trial was significantly ($P < 0.001$) different between the two soils (Table 7.2.i), with soil extractable Cd concentrations being approximately 4-times greater in the Topehaehae soil (85 µg kg^{-1}) than the Kereone soil (20 µg kg^{-1}). However, there was no significant effect ($P > 0.05$) of irrigation regime or of plant on extractable Cd concentration within the same soil. Separated in pre-irrigation (Table 7.2.ii) and +3 day (Table 7.2.iii) sample timing groupings, mean soil extractable Cd concentrations were consistently greater for the +3 day samples relative to the pre-irrigation samples, however these differences only reached significance ($P < 0.05$) for treatments within the Kereone soil (Table 7.2.iv).

For individual 14-day irrigation cycles, the difference between +3 day and pre-irrigation samples (Table 7.3) showed no clear trend and highlighted that soil type provided the overriding treatment effect. Few instances occurred where flooded/non-flooded or planted/unplanted sub-treatments within a soil type were significantly different, and where this did occur there was little consistency between samplings.

Table 7.2. Mean soil extractable Cd concentration (µg kg^{-1}) representing; **i)** Overall mean, **ii)** Mean of pre-irrigation samplings, **iii)** Mean of +3 day samplings, and **iv)** Mean difference between +3 day and pre-irrigation samplings; in addition to **v)** Mean plant tissue Cd concentration (mg kg^{-1} DM), **vi)** Plant yield (g DM pot^{-1}), and **vii)** Plant Cd uptake (µg Cd pot^{-1}). Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

Measure		Treatment								*P* value
		KPN	KUN	KPF	KUF	TPN	TUN	TPF	TUF	
Soil extractable Cd conc. (µg kg^{-1})	**i)** Overall mean	20.9(a)	21.1(a)	20.0(a)	18.5(a)	84.4(b)	89.3(b)	88.9(b)	86.1(b)	***
	Std. Error	0.7	0.7	0.8	0.8	3.4	3.4	3.5	3.4	
	n	88	87	88	84	86	88	87	84	
	ii) Pre-irrigation mean	19.3(a)	19.4(a)	17.9(a)	16.1(a)	83.0(b)	87.6(b)	85.4(b)	81.4(b)	***
	Std. Error	1.0	1.1	1.0	1.1	5.4	5.2	4.9	5.0	
	n	44	43	45	41	44	44	44	40	
	iii) +3 day mean	22.6(a)	22.7(a)	22.1(a)	20.7(a)	86.0(b)	91.0(b)	92.5(b)	90.4(b)	***
	Std. Error	1.0	0.9	1.2	1.1	4.1	4.3	4.9	4.6	
	n	44	44	43	43	42	44	43	44	
	iv) Difference *(iii-ii)*	3.1	3.2	3.9	4.7	4.4	3.1	7.4	8.2	*n.s.*
	Std. Error	0.9	0.9	0.9	0.9	3.0	2.7	2.7	2.3	
	P value (Pre-irrigation vs +3 day)	*	*	**	**	*n.s.*	*n.s.*	*n.s.*	*n.s.*	
v) Plant tissue Cd (mg kg^{-1} DM)	Mean	0.208(a)		0.384(ab)		0.650(c)		0.604(bc)		***
	Std. Error	0.059		0.077		0.054		0.068		
	n	5		5		5		5		
	Main effects:									
	- *Soil type*	***								
	- *Irrigation regime*	*n.s.*								
vi) Plant yield (g DM pot^{-1})	Mean	5.40(c)		2.70(ab)		4.02(bc)		1.51(a)		***
	Std. Error	0.57		0.29		0.30		0.16		
	Main effects:									
	- *Soil type*	*n.s.*								
	- *Irrigation regime*	***								
vii) Plant Cd uptake (µg Cd pot^{-1})	Mean	1.001(a)		1.020(a)		2.602(b)		0.880(a)		***
	Std. Error	0.224		0.182		0.280		0.056		
	Main effects:									
	- *Soil type*	*.								
	- *Irrigation regime*	*								

*P≤0.05 **P≤0.01 ***P≤0.001 n.s. = not significant. Treatment codes: K = Kereone, T = Topehaehae; P = Planted, U = Unplanted; N = Non-flooded, F = Flooded

Table 7.3. Treatment mean soil extractable Cd concentration (μg kg^{-1}) for pre-irrigation and +3 day soil samplings, for individual flood irrigation cycles. Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

Irrigation cycle	Sampling timing	Treatment								*P* value
		KPN	KUN	KPF	KUF	TPN	TUN	TPF	TUF	
1	Pre-irrigation	16.7(a)	16.3(a)	16.2(a)	16.3(a)	90.1(b)	93.8(b)	98.1(b)	97.5(b)	***
	+3 days	21.0(a)	20.4(a)	21.1(a)	18.3(a)	111.2(b)	104.9(b)	117.7(b)	113.3(b)	***
	Difference	4.3(ab)	4.1(a)	4.9(ab)	2.0(a)	21.1(b)	11.1(ab)	19.7(ab)	15.9(ab)	**
	P value	**	*	*	*n.s.*	**	*	**	*	
2	Pre-irrigation	19.8(a)	20.6(a)	21.4(a)	18.0(a)	108.0(b)	110.4(b)	108.2(b)	112.4(b)	***
	+3 days	27.4(a)	25.0(a)	30.6(a)	30.3(a)	106.6(b)	124.2(b)	122.8(b)	125.0(b)	***
	Difference	7.6	4.4	9.2	12.3	-1.4	13.8	14.6	12.6	*n.s.*
	P value	***	*n.s.*	***	***	*n.s.*	*n.s.*	**	**	
3	Pre-irrigation	27.0(a)	28.2(a)	24.4(a)	22.8(a)	128.4(b)	132.2(b)	124.6(b)	123.8(b)	***
	+3 days	27.2(a)	28.2(a)	30.8(a)	27.6(a)	123.0(b)	128.2(bc)	141.6(c)	137.2(bc)	***
	Difference	0.2(ab)	0.0(ab)	6.4(ab)	4.8(ab)	-5.4(a)	-4.0(a)	17.0(b)	13.5(ab)	**
	P value	*n.s.*	*n.s.*	*	*	*n.s.*	*n.s.*	*	*n.s.*	
4	Pre-irrigation	26.3(a)	27.4(a)	26.4(a)	26.0(a)	143.0(b)	144.6(b)	136.6(b)	125.3(b)	***
	+3 days	26.4(a)	24.0(a)	27.2(a)	23.6(a)	116.5(b)	116.8(b)	117.6(b)	109.6(b)	***
	Difference	0.1(b)	-3.4(b)	0.8(b)	-2.4(b)	-26.5(a)	-27.8(a)	-19.0(ab)	-15.7(ab)	***
	P value	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*	**	**	*n.s.*	
5	Pre-irrigation	23.8(a)	21.4(a)	20.2(a)	18.8(a)	61.6(b)	66.2(b)	62.0(b)	67.8(b)	***
	+3 days	24.8(a)	27.8(a)	27.6(a)	27.0(a)	83.0(b)	84.2(b)	80.2(b)	78.4(b)	***
	Difference	1.0(a)	6.4(ab)	7.4(ab)	8.3(ab)	21.4(b)	18(ab)	18.2(ab)	10.7(ab)	*
	P value	*n.s.*	*	**	***	*	*n.s.*	*	**	
6	Pre-irrigation	25.8(a)	25.5(a)	23.4(a)	22.6(a)	71.6(b)	78.8(b)	76.2(b)	73.2(b)	***
	+3 days	25.4(a)	27.0(a)	19.6(a)	22.4(a)	69.4(b)	69.8(b)	71.8(b)	72.2(b)	***
	Difference	-0.4(b)	1.5(b)	-3.8(b)	-0.2(b)	-2.2(b)	-9.0(a)	-4.4(b)	-1.0(b)	**
	P value	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*	
7	Pre-irrigation	12.8(a)	12.8(a)	12.0(a)	9.8(a)	57.6(c)	56.4(bc)	51.6(bc)	49.8(b)	***
	+3 days	26.0(a)	25.4(a)	20.0(a)	21.6(a)	69.6(bc)	64.6(b)	77.3(c)	74.8(c)	***
	Difference	13.2(ab)	12.6(ab)	8.0(a)	11.8(ab)	12.0(ab)	8.2(a)	25.7(b)	25.0(b)	***
	P value	***	***	***	***	**	*	***	***	
8	Pre-irrigation	9.8(a)	9.8(a)	9.8(a)	8.8(a)	42.6(b)	51.4(bc)	61.0(c)	49.8(bc)	***
	+3 days	10.8(a)	12.4(a)	9.2(a)	8.8(a)	53.4(b)	57.8(b)	51.8(b)	54.0(b)	***
	Difference	1.0	2.7	-0.6	0.0	10.8	6.4	-9.2	4.2	*n.s.*
	P value	*n.s.*	**	*n.s.*	*n.s.*	*	*n.s.*	*n.s.*	*n.s.*	
9	Pre-irrigation	13.0(b)	12.6(b)	8.0(ab)	6.6(a)	45.4(c)	53.0(d)	45.4(c)	44.0(c)	***
	+3 days	12.6(a)	13.4(a)	11.0(a)	10.6(a)	59.6(bc)	64.8(c)	54.8(b)	56.4(bc)	***
	Difference	-0.4(a)	0.8(ab)	3.0(ab)	4.0(abc)	14.2(c)	11.8(bc)	9.4(abc)	12.4(bc)	***
	P value	*n.s.*	*n.s.*	*n.s.*	**	**	***	**	*	

*P≤0.05 **P≤0.01 ***P≤0.001 *n.s. = not significant*

Within individual irrigation cycles, the difference between +3 day and pre-irrigation mean soil extractable Cd concentrations for individual treatments reached significance in 39 comparisons (Table 7.3). Of these, 36 comparisons (92%) showed significantly greater soil extractable Cd concentration at +3 days relative to pre-irrigation.

7.4.2 Soil extractable Cd concentration over time

Figure 7.3 presents a graphical comparison of the mean soil extractable Cd concentration at each sampling date for the flooded and non-flooded treatments of the Topehaehae planted, Topehaehae unplanted, Kereone planted and Kereone unplanted treatments (Figure 7.3.a, b, c & d, respectively). The trend for greater soil extractable Cd concentrations at +3 day samplings relative to the pre-irrigation samplings in both flooded and non-flooded treatments is illustrated in these graphs. Within all treatments, there is a general increase in soil extractable Cd concentrations over the first 4-6 weeks of the trial. This phase is then followed by a decrease in soil extractable Cd concentration, with the Topehaehae soil in particular showing an abrupt 50-60% decrease over day 42-56 (Figure 7.3.a & b). Although not as abrupt, a similar trend was seen for the Kereone soil (Figure 7.3.c & d) where an approximate 60% decrease in soil extractable Cd concentration occurred over the latter half of the trial. This decline was not an effect of plant uptake, since soil extractable Cd concentrations in non-planted treatments showed the exact same patterns as the planted treatments throughout the trial.

7.4.3 Plantain tissue Cd concentration, yield and Cd uptake

Significant ($P < 0.001$) differences in overall treatment mean plantain tissue Cd concentrations were apparent (Table 7.2.v) with mean tissue Cd concentrations decreasing in the order Topehaehae non-flooded > Topehaehae flooded > Kereone flooded > Kereone non-flooded. However, the main effect was that of soil type ($P < 0.001$) with plant tissue Cd concentrations for the Topehaehae soil being approximately double those for the Kereone soil. In contrast, the main effect of irrigation regime on tissue Cd concentration was not significant ($P > 0.05$).

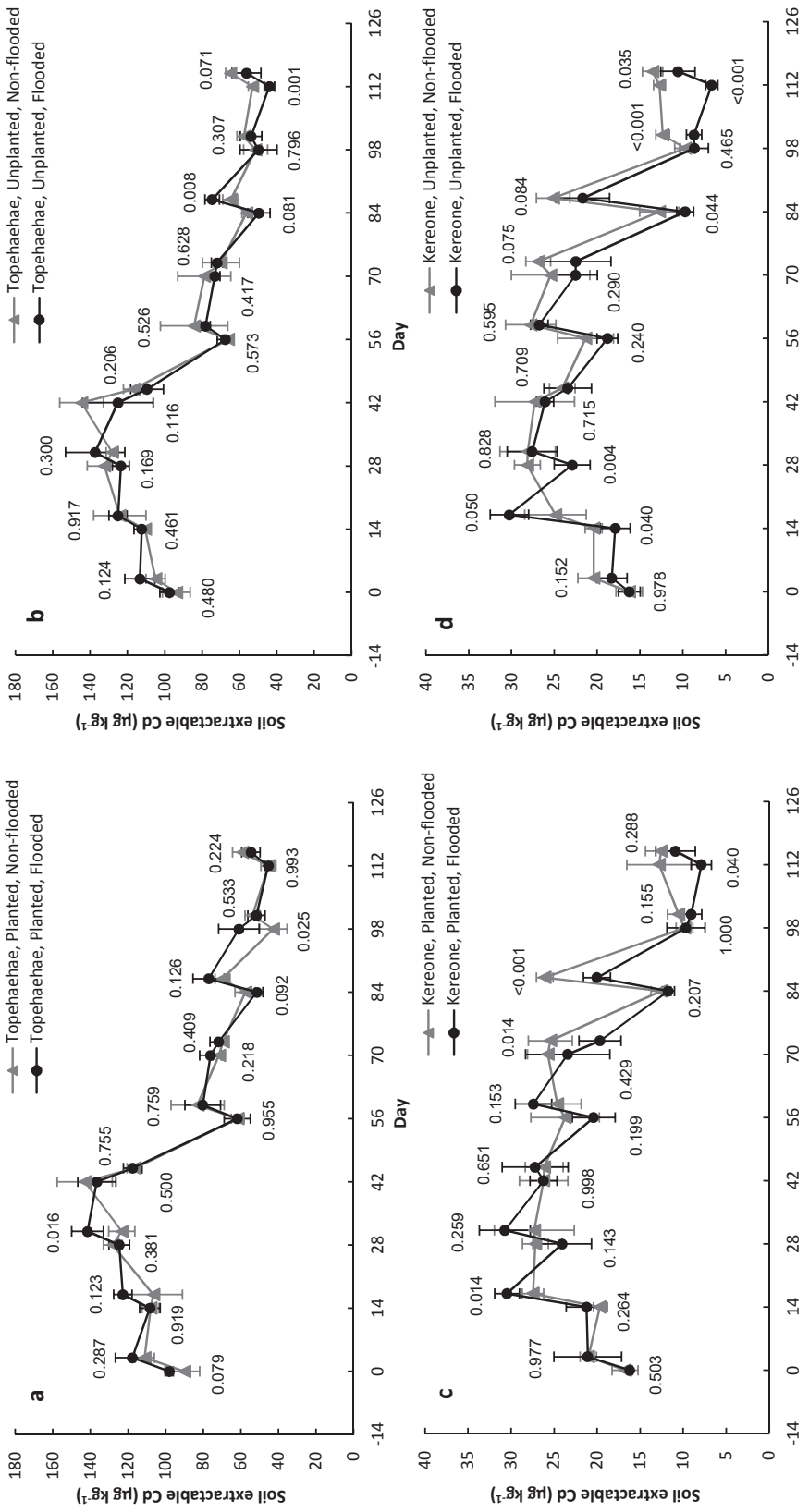

Figure 7.3. Mean 0.05 M $CaCl_2$ soil extractable Cd concentrations (µg kg^{-1}) at each sampling date under Flooded and Non-flooded conditions for **a)** Topehaehae Planted, **b)** Topehaehae Unplanted, **c)** Kereone Planted, and **d)** Kereone Unplanted treatments. ANOVA *P* values are provided for comparison of means at each sampling date. Error bars represent the 95% confidence interval.

Dry matter yield of plantain was significantly ($P < 0.001$) influenced by irrigation regime, however there was no relationship ($P > 0.05$) to soil type (Table 7.2.vi). Within the Kereone soil, an inverse relationship existed between plant yield and tissue Cd concentration, such that total Cd uptake was not significantly ($P > 0.05$) different for the flooded and non-flooded treatments (Table 7.2.vii). In contrast, in the Topehaehae soil, tissue Cd concentrations did not appear to be influenced by yield, and as a consequence total Cd uptake was significantly ($P < 0.05$) greater in the higher yielding non-flooded treatment.

7.5 Discussion

7.5.1 Change in soil extractable Cd as a function of irrigation events

This research indicates that the solubility of soil Cd is sensitive to initial increases in soil moisture content following periods of soil drainage, but is insensitive to short-term periods of soil saturation. This is shown by the relatively consistent increases in soil extractable Cd concentrations measured at the +3 day sampling timing relative to pre-irrigation, regardless of irrigation strategy (Figure 7.3 and Table 7.3).

Periodic pH assessment of 0.05 M $CaCl_2$ soil extracts throughout the trial indicated that there was no effect of irrigation regime on solution pH (Table 7.4). As change in redox potential is expected to influence soil solution pH (Gotoh and Patrick, 1972; Ponnamperuma, 1972; Gotoh and Patrick, 1974; Narteh and Sahrawat, 1999; DeLaune and Reddy, 2005) this suggests that either both soils buffered potential changes to soil pH brought about by differences in redox processes related to the two irrigation strategies, or alternatively, that the 3-day flooded period was insufficient for generating reducing soil conditions.

Table 7.4. pH of 0.05 M $CaCl_2$ extracts assessed periodically throughout the trial. Means with the same letter indicate differences are not significant from one another ($P < 0.05$).

Treatment	Day of sampling				*P* value
	0	28	84	112	
KPN	4.04	4.09 (ab)	4.29	4.44	
KPF	3.94	4.28 (b)	4.38	4.27	
TPN	3.97	4.00 (a)	4.17	4.23	
TPF	3.92	4.10 (ab)	4.13	4.12	
P value	*0.150*	*0.042*	*0.294*	*0.144*	
Sampling mean	3.97 (a)	4.11 (ab)	4.24 (b)	4.27 (b)	*<0.001*

As redox potential is known to change within a few days of saturation (Ponnamperuma, 1972) differences in soil redox behaviour should have been established by the contrasting irrigation regimes used in this study. Notably, Bhatti *et al.* (2013) employed very similar irrigation methodology to that used in this study, and reported significant increases in plant As concentration under flooded compared to non-flooded irrigation treatments, which they attributed to the dissolution of Fe hydrous oxides under the short-term flooded conditions. In contrast to the findings of Bhatti *et al.* (2013), plant Cd concentrations did not show significant differences between flooded and non-flooded irrigation regimes in this trial, providing further evidence that Cd phytoavailability is not sensitive to short-term periods of soil saturation.

Dissolution of Mn hydrous oxides can occur even under oxidising conditions when soil pH is mildly acidic (Gotoh and Patrick, 1972). Given both the Topehaehae and Kereone soils had mildly acidic soil pH at the time of soil collection (pH 5.6 and 6.3, respectively; Table 7.1) it is possible that the lack of difference in extractable Cd concentration patterns between flooded and non-flooded treatments may be related to Mn hydrous oxide dissolution with increased soil moisture, regardless of irrigation regime.

7.5.2 Change in soil extractable Cd as a function of time

This study is the first to evaluate changes in Cd solubility over time under contrasting wetting/drying soil moisture cycles. A large increase in soil extractable Cd concentration was recorded over the first 4-6 weeks of the trial, followed by a large (50-60%) decrease thereafter,

which was consistent for both irrigation regimes and soil types (Figure 7.3). Data presented in Figure 7.3 indicates that in the initial 4-6 weeks of the trial, the increase in soil extractable Cd concentrations that occurred between each pre-irrigation and +3 day sampling was not reversed (or completely reversed) over the subsequent drained phase, resulting in successively greater soil extractable Cd concentrations at each subsequent pre-irrigation sampling. With relatively dry soil conditions at the time of soil collection (gravimetric moisture content (θ_m) for both soils of ~0.42 g g^{-1}, compared to θ_m at Fc_P of 0.64 and 0.73 g g^{-1} for the Topehaehae and Kereone soils, respectively) it is possible that the trend for increasing soil extractable Cd concentrations over the first 4-6 weeks of the trial was a consequence of an abrupt increase in soil moisture driving re-equilibration of soil extractable Cd, following the initiation of regular irrigation inputs. As soil organic matter is an important sink for Cd in New Zealand agricultural soils (Gray *et al.*, 2000) it is also possible that mineralisation of soil organic matter following sieving/potting may have reduced the soils Cd sorption potential, thereby increasing labile-Cd during the first 4-6 weeks of this study.

The consistent decline in soil extractable Cd concentrations that occurred beyond day 42-56 coincides with a small but significant ($P < 0.001$) increase in the pH of 0.05 M $CaCl_2$ soil extracts that occurred during the course of the trial (Table 7.4). With an increase in pH, specific sorption of Cd would be expected to increase with a corresponding decrease in Cd phytoavailability (McBride, 1989; Naidu *et al.*, 1994; Bolan *et al.*, 1999b; Loganathan *et al.*, 2012). The increase in soil solution pH is therefore consistent with the decrease in soil extractable Cd concentrations measured mid-way through the trial. This does not contradict the increase in soil extractable Cd concentrations observed during the initial 4-6 weeks (Figure 7.3), since soil solution pH during this period did not change significantly (Table 7.4).

Alternatively, the decline in soil extractable Cd concentrations mid-way through the trial may have been temperature related. The decline aligns with the coldest period of winter when overnight temperatures regularly approached 0 °C (Figure 7.2). With a decrease in

temperature, a decrease in the decomposition rate of soil organic carbon is expected (Yamane and Sato, 1967). As a consequence of this decrease in energy availability, lower respiratory oxygen demand is likely to result in a decrease in microbially-induced reduction (Lovley, 1995). Hindersmann and Mansfeldt (2014) reported an inverse relationship between temperature and the time taken to transition from oxidising to weakly reducing soil conditions, noting an increase from 10 to 160 hours at temperatures of 15 °C and 7 °C, respectively. In this trial, with the maximum soil saturation period being only 3 days, it may be that oxidising conditions remained prevalent over the cooler winter period in all treatments. Consequent precipitation of Mn and Fe oxides under oxidising soil conditions would result in greater specific sorption of Cd, possibly explaining the overall decline in soil extractable Cd concentrations beyond day 42.

7.5.3 Effect of soil type on Cd phytoavailability and uptake

Despite soil total Cd concentration being 30% greater in the Kereone soil than the Topehaehae soil (0.79 versus 0.61 mg kg^{-1}, respectively; Table 7.1) soil extractable Cd concentrations were around 4 times greater in the Topehaehae soil (Table 7.2). Correspondingly, tissue Cd concentrations were also greater (approximately double) for plantain grown in the Topehaehae soil than the Kereone soil (Table 7.2).

Although an inverse relationship between tissue Cd concentration and plant yield is frequently reported in the literature (Mortvedt *et al.*, 1981; Loganathan *et al.*, 1997; Roberts and Longhurst, 2002) this effect was only evident in the Kereone soil, resulting in equivalent plant Cd uptake between low-yielding flooded and high-yielding non-flooded irrigation regimes. In contrast, the greater extractable Cd concentrations of the Topehaehae soil sustained plant tissue Cd concentration irrespective of the differing plant growth rate under the two irrigation regimes, resulting in much greater plant Cd uptake for the higher-yielding non-flooded treatment. The observation that tissue Cd dilution with increasing growth rate only occurred at low Cd phytoavailability is consistent with the finding of Mortvedt *et al.* (1981).

The differences in Cd phytoavailability between the two soils types can be explained by differences in soil characteristics. Although cation exchange capacity, Mn oxide and Fe and Al amorphous oxide content have been shown to be correlated with soil Cd desorption, soil total Cd, pH and organic matter content have found to be the dominant factors regulating Cd solubility and desorption (Gray *et al.*, 1999d). Of these three factors, total Cd is positively correlated while soil pH and organic matter are negatively correlated (McBride *et al.*, 1997; Gray *et al.*, 1999d). The overriding effect of soil pH on metal phytoavailability is regularly cited in the literature, particularly for soils with high variable charge capacity such as those in this study (Naidu *et al.*, 1997; Bolan *et al.*, 1999b; Loganathan *et al.*, 2012). Notably, the pH of the Topehaehae soil was 0.7 pH units lower than that of the Kereone soil at the outset of the trial. The greater pH of the Kereone soil, coupled with its greater organic matter content and predominance of variable charge clays (especially allophane and Mn oxides) is likely to explain the much lower extractable Cd concentrations of this soil type.

The importance of soil pH and organic matter content in regulating soil Cd solubility was demonstrated by Gray *et al.* (1999d) who developed an algorithm (Equation 1) that accounted for 76% of the variation in soil solution Cd concentrations of 29 New Zealand soils:

$$Log[Cd]_S = 7.28 - 0.89pH + 1.21LogCd_T - 1.04LogOM \quad (1)$$

Where *Log* refers to base-10 logarithms for Cd_S (Cd concentration in soil solution, µg L^{-1}), Cd_T (soil total Cd concentration, mg kg^{-1}) and *OM* (soil organic matter, g kg^{-1}).

Using Equation 1, based on the soil pH, carbon and total Cd values in Table 7.1 (carbon being converted to soil organic matter using the Van Bremmelen factor of 1.724 (Tan, 2005)) soil solution Cd concentrations were predicted to be approximately 5-6 times greater for the Topehaehae soil than the Kereone soil (Table 7.5). In relative terms, this is similar to the difference in mean soil extractable Cd concentrations measured for the Topehaehae and

Kereone soils (Table 7.2) demonstrating the importance of soil pH and organic matter content in regulating phytoavailability of soil total Cd.

Table 7.5. Prediction of soil solution Cd concentrations for the soils in this study based upon total Cd, organic matter and pH, using the Cd solubility equation of Gray *et al.* (1999d).

Soil	pH	$LogCd_T$ (mg kg^{-1})	LogOM (g kg^{-1})	$Log[Cd]_S$ (µg L^{-1})	Cd_S (µg L^{-1})
Kereone	6.3	-0.102	-0.008	1.557	36.06
Topehaehae	5.6	-0.215	-0.258	2.305	201.79

7.5.4 Implication of these findings to Cd management in agricultural soils

The trend shown in this trial for increases in soil extractable Cd concentration with increases in soil moisture is a new and potentially important finding with regard to Cd management in agricultural soils. This observation suggests that after a period of drainage or soil drying, soil Cd phytoavailability is sensitive to subsequent rainfall or irrigation inputs, and indicates that Cd phytoavailability increases with increasing soil moisture prior to the point of saturation and the associated onset of reducing soil conditions.

This new knowledge may provide greater insight into appropriate soil Cd management strategies for minimising livestock dietary Cd exposure. For example, under typical New Zealand non-irrigated pastoral agriculture conditions, chicory and plantain crops are planted to provide quality feed when ryegrass-white clover based pastures are compromised by hot, dry summer to early-autumn conditions (Somasiri *et al.*, 2015). As chicory and plantain have been shown to be 'Cd-accumulator' species (Stafford *et al.*, 2016) it is likely that their tissue Cd concentrations will be enriched following rainfall events that substantially increase soil moisture during the predominantly dry summer and autumn soil conditions. This effect has been observed in recent field trials investigating Cd accumulation in chicory (see Chapter 8). Consistent across two contrasting soils, mean tissue Cd concentrations were significantly ($P < 0.05$) greater at the 2nd harvest (3.56-4.67 mg kg^{-1} DM) relative to the 1st (1.45-1.53 mg kg^{-1} DM) and 3rd (1.81-2.03 mg kg^{-1} DM) harvests. Notably, a large rainfall event (23 mm rainfall

within 24 hours) occurred during the 2nd growth cycle that rewet the topsoil. In contrast, rainfall was infrequent and of low intensity during the 1st growth cycle, while only 1 mm of rainfall arrived during the entirety of the 3rd growth cycle.

Practically, there is little ability to avoid grazing these crops following periods of increased soil moisture. Hence, where these Cd-sensitive crops are to be sown in Cd-enriched soil, management interventions should be explored to minimise potential increases in Cd phytoavailability that will be aligned with periods of increased soil moisture. As soil pH is considered one of the single most important factors influencing Cd sorption-desorption behaviour and solubility (Bolan *et al.*, 1999b; Christensen and Haung, 1999; Gray *et al.*, 1999d; Loganathan *et al.*, 2012; Young, 2012) managing soil pH at the upper end of the optimum range for these crops would be a logical starting point. However, the effect of increasing soil pH on Cd accumulation in plantain and chicory has yet to be quantified in field trials. Furthermore, although sorption of Cd is known to increase with increasing soil pH with a concurrent shift towards less labile, specifically-sorbed Cd (Naidu *et al.*, 1994; Bolan *et al.*, 2003c; Loganathan *et al.*, 2012), the assumption that this will reduce the size of the soil Cd fraction mobilised during periods of increased soil moisture needs to be proven. Further research in this area is warranted, as the mechanisms behind the increases in Cd phytoavailability that were seen in this study that paralleled increases in soil moisture are not yet fully understand.

Outside of modification of soil pH, it may be possible to modify tillage and irrigation practice (where applicable) to manage the effects of soil moisture driven changes in Cd phytoavailability. Cadmium tends to be non-uniformly distributed in the soil profile with greater concentrations found near the soil surface (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999). As such, the majority of soil Cd is found in the topsoil zone that is subject to the greatest fluctuations in soil moisture. Burial of Cd-enriched topsoil via deep 'inversion-tillage' (Angers and Eriksen-Hamel, 2008; Lawrence-

Smith *et al.*, 2015) is likely to reduce overall soil Cd phytoavailability, and in addition, it will also move Cd-enriched topsoil away from the soil surface. As a consequence, its phytoavailability will be less influenced by temporary fluctuations in soil moisture resulting from sporadic rainfall events. Deep inversion-tillage may also be a suitable management practice for managing Cd accumulation in Cd-sensitive food crops such as lettuce and spinach (Singh and Nayyar, 1990; Gray *et al.*, 1999a, c; Bešter *et al.*, 2013). Furthermore, for these high-value food crops, it may be possible to regulate soil moisture with controlled surface or subsurface irrigation, so as to avoid sudden increases in Cd phytoavailability near to the time of harvest.

7.6 Conclusions

The results from this pot trial indicate that temporary fluctuations in soil moisture content can influence soil Cd phytoavailability, with increases in soil extractable Cd concentration paralleling increases in soil moisture content. However, soil saturation for short periods (3 days) did not appear to exert any influence on soil Cd phytoavailability, relative to continuously drained conditions. The data from this trial suggests that plant tissue Cd concentrations are likely to be enriched in Cd-accumulator crops (such as chicory and plantain) during periods where soil moisture is abruptly increased following a period of drying. Potentially, this risk may be managed through a combination of deep inversion-tillage (to transfer Cd-enriched topsoil deeper into the soil profile where it is less accessible to plant roots, and where it will be less influenced by soil moisture fluctuations near the soil surface), manipulation of soil pH (increase pH to drive greater specific sorption of Cd) and where possible, controlled irrigation to avoid over watering near to the time of grazing or harvest. The results from this trial also reinforce that factors such as soil pH and organic matter content that regulate Cd solubility need to be incorporated into Cd management frameworks, where the objective is to minimise plant Cd accumulation.

CHAPTER 8 : Cadmium accumulation in chicory and ryegrass with modification of pH in two soils

8.1 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*). Averaged over three harvests, 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. Chicory tissue Cd concentrations were significantly ($P < 0.05$) greater at the 2nd harvest, coinciding with a large rainfall event that occurred midway through that growth cycle. In contrast, soils were relatively dry during the 1st and 3rd harvest growth cycles. These findings reinforce previous pot trial observations that indicated increased soil Cd phytoavailability when soils rewet following periods of drying. As tissue Cd concentrations in ryegrass remained low (<0.3 mg kg^{-1}) in the Cd-enriched Kereone soil across

the entire pH range imposed, there appears little risk of increased animal dietary Cd exposure related to low soil pH when grazing this plant species. In contrast, this trial reinforces that for Cd accumulating crops such as chicory, soil pH should be increased to a minimum pH of 6.5 to decrease tissue Cd accumulation.

8.2 Introduction

Soil pH is generally considered to be the dominating factor influencing metal sorption and solubility in soils (Bolan *et al.*, 1999b; Christensen and Haung, 1999; Gray *et al.*, 1999d; 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, 1999c, d; 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.*, 2003c; 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.*, 1999c; 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.*, 1993a; 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.*, 1993a; 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.*, 1999c). 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.*, 2003c).

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, under the Tiered Fertiliser Management System (MAF, 2011; Cavanagh, 2012) 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 'Cd-accumulator' crops, as exemplified in Chapter 4 by chicory (*Cichorium intybus*). Notably, data from a recent survey of plant tissue and soil samples collected from commercial farming properties across New Zealand (Chapter 5) 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. However, as all three parameters (soil total Cd, total C and pH) vary within the survey dataset, controlled trials are necessary to isolate and validate the influence of soil pH on tissue Cd accumulation in chicory, while allowing total Cd and total C to remain constant. The field research trial in this chapter was therefore undertaken to benchmark Cd accumulation in chicory against ryegrass in two contrasting soils (Kereone silt loam and the Topehaehae sandy clay loam) with the modification of soil pH using varying rates of ultra-fine elemental sulphur or calcium hydroxide.

8.3 Methodology

8.3.1 Field trial

To assess the effect of modifying soil pH on soil extractable Cd concentrations as well as Cd accumulation in chicory and ryegrass, two trials were established on contrasting soils within the Waikato case study farm. Upon initial reconnaissance and following discussion with the farm owner, for practicality purposes (i.e. ease of access, and to fit in with day-to-day farm management) it was decided to locate both trial sites within paddocks 1 and 2 of the original dairy farm, immediately adjacent to the roadside entrance of the property (Chapter 3, Figure 3.3). Detailed soil profile descriptions for the Kereone silt loam and the Topehaehae sandy clay loam soil types represented at these site locations can be found in Appendix 1, Section A1.1.1 and A1.1.2). Suitable sites within these paddocks (e.g. uniform topography) were pegged out, with soil samples taken across the entirety of both trial areas. The characteristics of the two soil types used in this study are provided in Table 8.1, with the relevant analytical methodologies described in Section 8.3.2 and Appendix 2.

Table 8.1. 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

8.3.1.1 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 8.2. 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 8.2. 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 (Appendix 2, Table A2.1 and Table A2.2). However, these theoretical calculations were much lower than the rates of lime required in practice (Morton *et al.*, 1998b; Morton *et al.*, 2005; Moir and Moot, 2014) and 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. Despite differing pH buffering capacities of the two soil types in this soil, no differentiation was made as to the rates of hydrated lime / elemental sulphur that were applied to the two soils. This decision was made based on uncertainty as to the magnitude of

the pH change that would be generated, and since the main objective was to ensure a range of pH values was generated, rather than a specific pH value per se.

8.3.1.2 Management

On 11 September 2015 the two trial sites were fenced-off (Figure 8.1) 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 (Figure 8.2.a). 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 (Lolium perenne; cultivar Excess® (PGG Wrightson seeds) with AR 37® endophyte and Superstrike® insecticide coating) and chicory (Cichorium intybus; cultivar 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.

Rabbits were shot on several occasions to decrease high populations in surrounding paddocks, which were observed to be causing damage to some chicory and ryegrass plots. However, despite following best practice (AR 37® endophyte and Superstrike® insecticide seed coating) high damage was caused by Black Beetle (*Heteronychus arator*; common to the northern North Island of New Zealand) to ryegrass plots on the free-draining Kereone soil site. Although numerous dead Black Beetle were evident as a consequence of the plant-defence afforded by insecticide and endophyte, with no insecticide-spray option available to control this insect pest, the only option to counter losses in plant population was to apply more ryegrass seed (undertaken on 31 October 2015). Although rainfall up until this point had been uncharacteristically infrequent and light (Figure 8.3) good rainfall occurred within a few days of ryegrass seed reapplication, promoting rapid germination and establishment over the

subsequent weeks. However, ryegrass yield at the first harvest was still compromised in the Kereone soil.

8.3.1.2.1 Plant tissue harvests

Three plant tissue harvests took place through the trial duration, occurring on 18 November, 11 December (Figure 8.2.b) 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. Care was taken to avoid collecting plants near the outer perimeter of each plot, where 'edge-effects' were more likely (e.g. due to reduced plant competition and greater sunlight exposure and soil moisture availability). Plant tissue replicate samples were placed in paper bags upon collection, with fresh weights being immediately recorded.

At each harvest, the total vegetative biomass in each 4 m^2 plot area was assessed by harvesting with a hand mower to approximately 30 mm height. Fresh weight yields were recorded in the field, which were later converted to dry matter yield using the treatment-mean dry matter value (% DM) from the hand-cut tissue samples collected for Cd analysis. This provided a non-replicated yield value for each treatment at each harvest.

8.3.1.2.1 Soil sampling

To check for establishment of acid / alkali treatment effects on soil pH and extractable Cd concentrations, a trial 'mid-point' soil sampling occurred on 24 November 2015. For this purpose, only treatments 11, 16 and 20 (Table 8.2) were sampled within each site. Three

replicates (each consisting of five soil cores taken to 150 mm soil depth) were collected in parallel lines within each treatment plot. These samples were couriered to Massey University where they were immediately analysed for extractable Cd concentration and pH.

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.

Figure 8.1. Site selection for the trials sites located on the **a)** Kereone, and **b)** Topehaehae soil. In the top photo, the Topehaehae site can be seen next to the fence line in front of the trees and creek in the distant, lower-lying part of the paddock (photographs courtesy of the author).

Figure 8.2.a) Application of hydrated lime and elemental sulphur treatments to individual plots at the Topehaehae trial site, and **b)** harvest 2 (11 December 2015) of the Topehaehae trial site (photographs courtesy of the author).

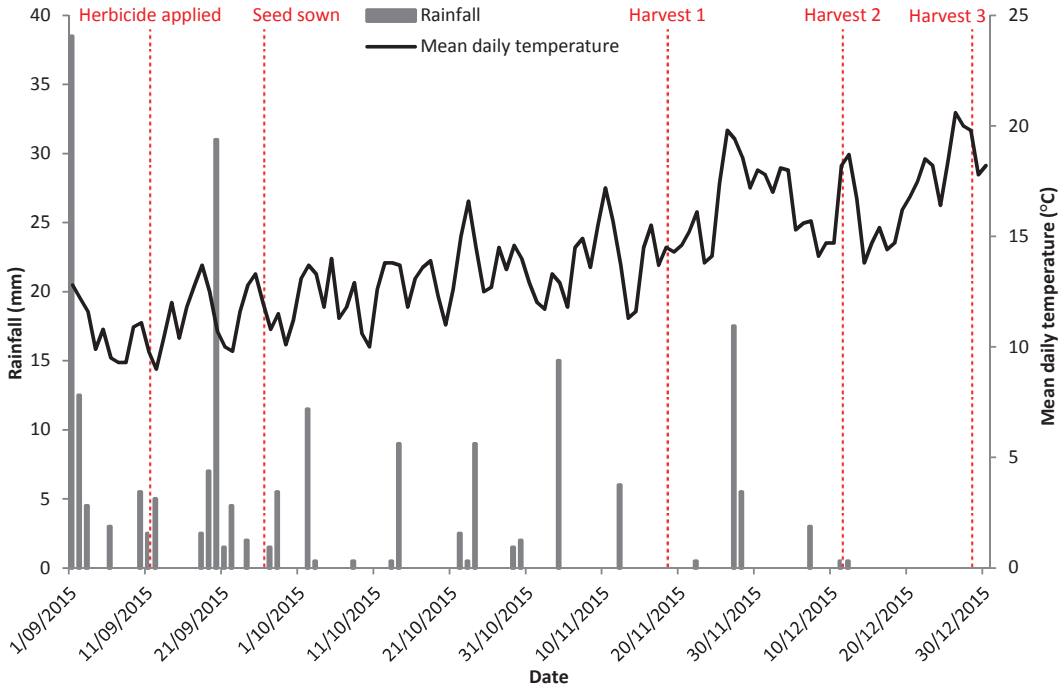

Figure 8.3. Rainfall and temperature profile for the district where the trial site was located (Rainfall data: Matamata aerodrome, courtesy of Waikato Regional Council); temperature data: NIWA 'CliFlo' climate station 23908).

8.3.2 Chemical analysis

8.3.2.1 Plant tissue Cd and soil extractable Cd

Analytical methodology for plant tissue Cd concentration and soil extractable Cd concentration can be found in Chapter 7 (Sections 7.3.5.1 and 7.3.5.2, respectively).

8.3.2.2 Soil pH

Soil pH analysis was based on that described by Blakemore *et al.* (1987). Briefly, 25 mL of deionised water was added to 10 mL of ground, air-dried soil to provide a 1:2.5 (v/v) soil to water slurry, which was then left to stand overnight. Without stirring, solution pH was measured the following day using a Eutech Instruments CyberScan pH 310 fitted with an Ag/AgCl oxidation reduction potential reference electrode.

8.3.2.3 Soil pH buffer capacity

Soil pH buffer capacity analysis was derived from the methodology of Russo and Hanania (1987). Following this approach, dried and sieved (<2 mm) soil subsamples (20 g) were deposited into a set of ten 120 mL plastic beakers. Into these beakers, 2, 3, 4, 5 or 6 mL of 0.2 M NaOH, or 0, 1, 2, 4 or 6 mL of 0.2 M HCl was added, along with the required amount of deionised water to total 8 mL of added solution. The soil was then left to incubate at room temperature for 30 minutes, before a further 42 mL of water was added to each beaker to make up a 1:2.5 soil:solution suspension. This suspension was then stirred and left for 30 minutes to equilibrate, before pH measurements were made using the same equipment described previously (Section 8.3.2.2). For each soil, the amount of H^+ or OH^- added was then plotted against soil pH, with the slope of the graph between pH 5-7 used to define the pH buffer capacity of the two soils (Appendix 2, Figure A2.1 and Figure A2.2).

8.3.2.4 Other soil analysis

Initial soil analysis to characterise the soil at each site prior to trial establishment was carried out at Hill Laboratories (1 Clyde Street, Hamilton). Detailed analytical methodology is provided in Chapter 3 for these tests, which include: total Cd (Section 3.4.4.1), total P (Section 3.4.4.2), total C (Section 3.4.4.3), plant available P (Olsen-P, Section 3.4.4.4), pH (Section 3.4.4.5), phosphate retention (P retention, Section 3.4.4.6) and cation exchange capacity (CEC, Section 3.4.4.7).

8.3.3 Statistical analysis

Statistical analysis was carried out using the software SPSS (IBM Corp, 2013). Analysis of variance (ANOVA) was undertaken to assess for differences in soil type, plant species, individual harvest and alkali/acid treatment means, while Tukeys honestly significant difference (HSD) was run as a post-hoc analysis to identify differences between individual means. Using all individual replicate samples, multiple regression analysis was undertaken to

evaluate the relationship between soil extractable Cd concentration and the variables soil type, soil pH, and plant species. Linear regression analysis was also used to describe the relationship between soil extractable Cd concentration and soil pH, as well as plant tissue Cd concentration and soil pH or soil extractable Cd concentration.

8.4 Results

8.4.1 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 8.3). The greater soil extractable Cd concentration of the Kereone soil is consistent with its much greater soil total Cd concentration (Table 8.1).

Table 8.3. 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*	

Ryegrass mean tissue Cd concentration was significantly (P = 0.036) greater in the Kereone than the Topehaehae soil (Figure 8.3), consistent with the greater soil extractable Cd concentration of the Kereone soil. Although the mean tissue Cd concentration for chicory was greater for the Topehaehae soil than the Kereone soil, this difference was not significant (P = 0.217). Mean tissue Cd concentrations in control plots were significantly greater (P < 0.001) for chicory (1.643-2.413 mg kg^{-1} DM) than ryegrass (0.062-0.111 mg kg^{-1} DM).

8.4.2 Main treatment effects

In both the Kereone (Table 8.4) and Topehaehae (Table 8.5) soils, treatment mean soil pH and extractable Cd concentrations assessed at the final harvest were significantly ($P < 0.001$) influenced by the varying rates of calcium hydroxide and elemental sulphur. Elemental sulphur treatments consistently drove significant ($P < 0.05$) reductions in soil pH (relative to that of the control) in both soils (Table 8.4 and Table 8.5) with the exception of the lowest application rate of elemental sulphur (0.5x acid) on the chicory plots of the Kereone soil (Table 8.4). Although elemental sulphur treatments generally increased soil extractable Cd concentration, this treatment effect was more variable than for soil pH, with fewer instances where soil extractable Cd concentration was significantly ($P < 0.05$) different to the control.

With the exception of the greatest rate of hydrated lime on chicory plots in the Topehaehae soil (Table 8.5), hydrated lime treatments did not drive significant increases in soil pH in either soil (Table 8.4 and Table 8.5). However, despite the lack of significance, there was a consistent trend in the Topehaehae soil for pH to increase with increasing rate of hydrated lime (with the exception of the '0.5x alkali' treatment where there was a non-significant but consistent decrease in pH relative to the control). This rate of hydrated lime versus pH trend was not present in the Kereone soil, likely due to its greater pH buffering capacity (Table 8.1).

No hydrated lime treatments significantly decreased soil extractable Cd concentration relative to the control in either soil, although significant ($P > 0.05$) increases in soil extractable Cd concentration were observed for the lowest rate of hydrated lime (0.5x alkali) for ryegrass in the Kereone soil (Table 8.4) and for both plant species in the Topehaehae soil (Table 8.5). This is consistent with the apparent (non-significant) decrease in pH relative to the control that was observed for the lowest rate of hydrated lime (0.5x alkali) in both soils.

Table 8.4. Kereone site treatment mean soil pH and extractable Cd concentration (mg kg^{-1}) as assessed at the final harvest, and mean tissue Cd concentration (mg kg^{-1} DM) and total yield (kg DM ha^{-1}) for chicory and ryegrass assessed over three harvests. Means followed by the same letter are not significantly different from one another ($P < 0.05$).

Treatment No.	Species	Alkali / acid treatment	Soil pH	Soil extractable Cd conc. (mg kg^{-1})	Mean plant tissue Cd conc. (mg kg^{-1} DM)	Total yield (kg DM ha^{-1})
1	Chicory	Control	5.95(de)	0.124(abcde)	1.643(c)	4512
2	Chicory	0.5x alkali	5.76(cd)	0.174(defgh)	2.193(cd)	5175
3	Chicory	1x alkali	5.95(de)	0.114(abcde)	1.852(c)	5417
4	Chicory	2x alkali	5.97(de)	0.117(abcde)	1.894(c)	4658
5	Chicory	3x alkali	5.86(de)	0.161(cdefg)	2.429(cd)	4630
6	Chicory	4x alkali	5.88(de)	0.123(abcde)	1.459(bc)	5562
7	Chicory	0.5x acid	5.96(de)	0.113(abcde)	1.940(c)	4669
8	Chicory	1x acid	5.25(a)	0.220(ghi)	3.174(d)	4978
9	Chicory	2x acid	5.36(a)	0.179(efghi)	3.286(d)	5469
10	Chicory	3x acid	5.38(a)	0.207(fghi)	2.629(cd)	4729
11	Ryegrass	Control	6.19(ef)	0.086(ab)	0.111(a)	2913
12	Ryegrass	0.5x alkali	5.86(de)	0.176(defghi)	0.118(a)	3000
13	Ryegrass	1x alkali	5.93(de)	0.142(bcdef)	0.103(a)	1865
14	Ryegrass	2x alkali	5.72(bcd)	0.170(defgh)	0.145(a)	3149
15	Ryegrass	3x alkali	6.11(ef)	0.107(abcd)	0.152(a)	2712
16	Ryegrass	4x alkali	6.44(f)	0.057(a)	0.098(a)	3038
17	Ryegrass	0.5x acid	5.50(abc)	0.246(i)	0.148(a)	3029
18	Ryegrass	1x acid	5.99(de)	0.091(abc)	0.102(a)	2536
19	Ryegrass	2x acid	5.29(a)	0.242(hi)	0.260(ab)	3095
20	Ryegrass	3x acid	5.23(a)	0.227(ghi)	0.195(a)	3458
21	Fallow	-	5.39(ab)	0.236(hi)	-	
		P value	*<0.001*	*<0.001*	*<0.001*	

Table 8.5. Topehaehae site treatment mean soil pH and extractable Cd concentration (mg kg^{-1}) as assessed at the final harvest, and mean tissue Cd concentration (mg kg^{-1} DM) and total yield (kg DM ha^{-1}) for chicory and ryegrass assessed over three harvests. Means followed by the same letter are not significantly different from one another ($P < 0.05$).

Treatment No.	Species	Alkali / acid treatment	Soil pH	Soil extractable Cd conc. (mg kg^{-1})	Mean plant tissue Cd conc. (mg kg^{-1} DM)	Total yield (kg DM ha^{-1})
1	Chicory	Control	5.88(efgh)	0.079(abcd)	2.413(bc)	5035
2	Chicory	0.5x alkali	5.70(defg)	0.193(fg)	2.546(bc)	5135
3	Chicory	1x alkali	5.90(fghi)	0.142(def)	2.296(bc)	4824
4	Chicory	2x alkali	6.04(hij)	0.086(abcd)	2.972(bc)	5253
5	Chicory	3x alkali	6.10(hij)	0.081(abcd)	1.943(abc)	5432
6	Chicory	4x alkali	6.26(j)	0.030(a)	1.573(ab)	5322
7	Chicory	0.5x acid	5.51(cd)	0.104(bcde)	3.528(c)	5732
8	Chicory	1x acid	5.49(bcd)	0.078(abcd)	2.490(bc)	4732
9	Chicory	2x acid	5.16(ab)	0.239(gh)	3.530(c)	5296
10	Chicory	3x acid	5.27(abc)	0.112(cde)	3.694(c)	4864
11	Ryegrass	Control	6.00(ghij)	0.047(abc)	0.062(a)	2637
12	Ryegrass	0.5x alkali	5.68(defg)	0.161(ef)	0.128(a)	3961
13	Ryegrass	1x alkali	6.05(hij)	0.053(abc)	0.113(a)	3267
14	Ryegrass	2x alkali	6.17(hij)	0.040(ab)	0.085(a)	4004
15	Ryegrass	3x alkali	6.19(hij)	0.030(a)	0.122(a)	3880
16	Ryegrass	4x alkali	6.24(ij)	0.059(abc)	0.087(a)	4093
17	Ryegrass	0.5x acid	5.57(cdef)	0.112(cde)	0.136(a)	3212
18	Ryegrass	1x acid	5.54(cde)	0.190(fg)	0.126(a)	3732
19	Ryegrass	2x acid	5.29(abc)	0.155(ef)	0.140(a)	3949
20	Ryegrass	3x acid	5.01(a)	0.283(h)	0.129(a)	4073
21	Fallow	-	5.50(bcd)	0.084(abcd)	-	
		P value	*<0.001*	*<0.001*	*<0.001*	

Significant ($P < 0.001$) differences were apparent between treatment-mean plant tissue Cd concentrations (assessed as the mean across all three harvests) for both soils (Table 8.4 and Table 8.5). However, the greatest difference in plant tissue Cd concentration was the significant difference between species ($P < 0.001$; Table 8.3) with treatment mean tissue Cd concentrations being much greater for chicory (range 1.459-3.694 mg kg^{-1} DM) than ryegrass (range 0.062-0.260 mg kg^{-1} DM). Within each species, there were very few significant effects on tissue Cd concentrations from the alkali/acid treatments. However, chicory was more sensitive to these treatments than ryegrass, with a trend for greater tissue Cd concentrations in the elemental sulphur (acid) treated plots, which reached significance ($P < 0.05$) in the '1x acid' and '2x acid' treatments in the Kereone soil (Table 8.4).

Chicory and ryegrass total dry matter yield (kg DM ha^{-1}) for the three harvests combined is provided for each alkali/acid treatment, for the Kereone soil (Table 8.4) and the Topehaehae soil (Table 8.5). No statistical analysis was performed since treatment-level yield was a non-replicated assessment. Total dry matter yield tended to be greater for chicory than ryegrass in both soils. However, there was no consistent trend to the yield of either species in either soil with respect to hydrated lime or elemental sulphur treatments.

8.4.2.1 Plant tissue Cd concentration over time

8.4.2.1.1 Chicory

Significant ($P < 0.001$) differences in chicory mean tissue Cd concentration (mg kg^{-1} DM) and mean yield (kg DM ha^{-1}) were apparent between harvests within each soil type (Table 8.6). For both soils, the mean tissue Cd concentration and the mean yield were both significantly ($P < 0.05$) greater at the second harvest than the first and third harvests, with no significant ($P > 0.05$) difference in yield or tissue Cd concentration between the first and third harvests.

Table 8.6. Chicory mean tissue Cd concentration (mg kg^{-1} DM) and mean yield (kg DM ha^{-1}) at each harvest, for both the Kereone and Topehaehae soil types.

Soil type	Chicory harvest	Mean tissue Cd conc. (mg kg^{-1} DM)	Mean yield (kg DM ha^{-1})	Mean daily growth rate (kg DM ha^{-1} day^{-1})
Kereone	1	1.526(a)	1195(a)	23
	2	3.555(b)	2485(b)	108
	3	1.814(a)	1299(a)	76
	P value	*<0.001*	*<0.001*	
Topehaehae	1	1.450(a)	1263(a)	24
	2	4.674(b)	2702(b)	117
	3	2.027(a)	1198(a)	70
	P value	*<0.001*	*<0.001*	

Mean chicory tissue Cd concentrations for all alkali / acid treatments at each harvest is presented for the Kereone and Topehaehae soils in Figure 8.4 and Figure 8.5, respectively. For the Kereone soil, mean tissue Cd concentrations ranged between 0.956-2.204 mg kg^{-1} DM, 2.303-5.375 mg kg^{-1} DM and 1.201-2.477 mg kg^{-1} DM, for the first, second and third harvests, respectively. The greatest range in tissue Cd concentrations ranges was also seen at the second harvest for the Topehaehae soil, with mean tissue Cd concentrations ranging between 0.734-2.343 mg kg^{-1} DM, 2.475-6.100 mg kg^{-1} DM and 1.365-2.974 mg kg^{-1} DM, for the first, second and third harvests, respectively.

Alkali/acid treatments had a significant effect on chicory mean tissue Cd concentration at all three harvests for the Kereone soil ($P < 0.001$ for harvest 1 and 3, and $P = 0.011$ for harvest 2). However, a significant ($P < 0.001$) treatment effect was only apparent for harvest 1 and 3 for the Topehaehae site. Application of hydrated lime appeared to have little influence on mean tissue Cd concentrations for chicory in the Kereone soil (Figure 8.4). In many instances, it appeared that application of hydrated lime increased Cd concentrations relative to the control, most notably at the second harvest where there was a consistent increase in tissue Cd across all alkali treatments; however these increases were not statistically significant ($P > 0.05$). Similarly, for the Topehaehae soil (Figure 8.5) chicory tissue Cd concentrations in hydrated lime treatments were not significantly ($P > 0.05$) different to those of the control. Isolated to the rates of hydrated lime, there was a general trend for tissue Cd concentrations to

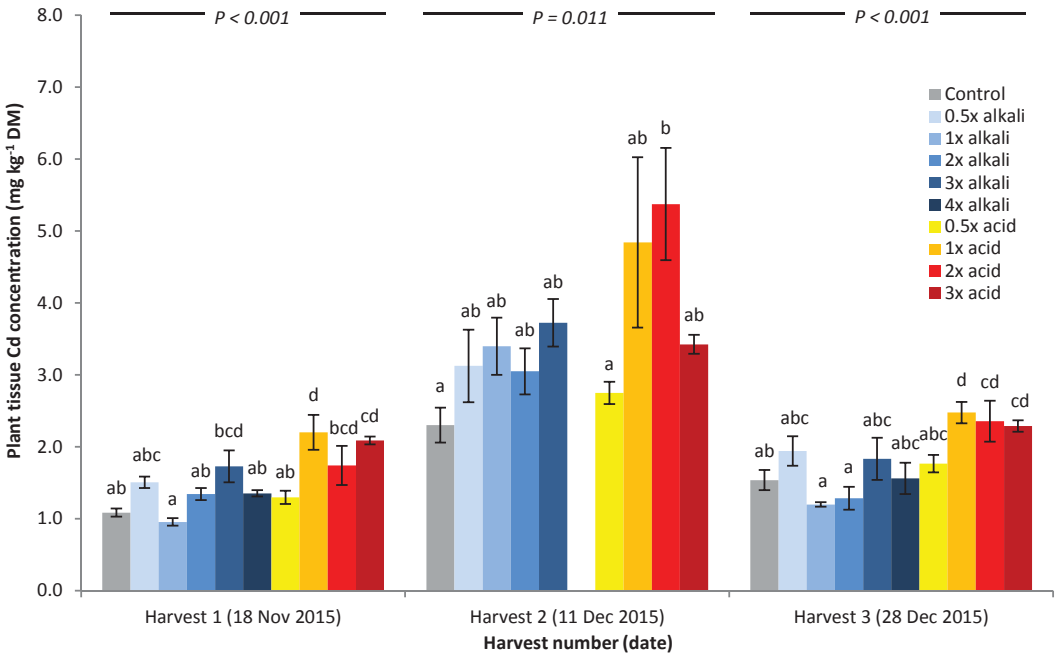

Figure 8.4. Mean chicory Cd concentrations for all alkali/acid treatments within the Kereone soil. Error bars represent the standard error. Treatment means within a harvest followed by the same letter are not significantly different from one another ($P < 0.05$). Note: Replicates of the '4x alkali' treatment from the 2nd harvest were lost prior to analysis, hence there is a missing data point for this treatment.

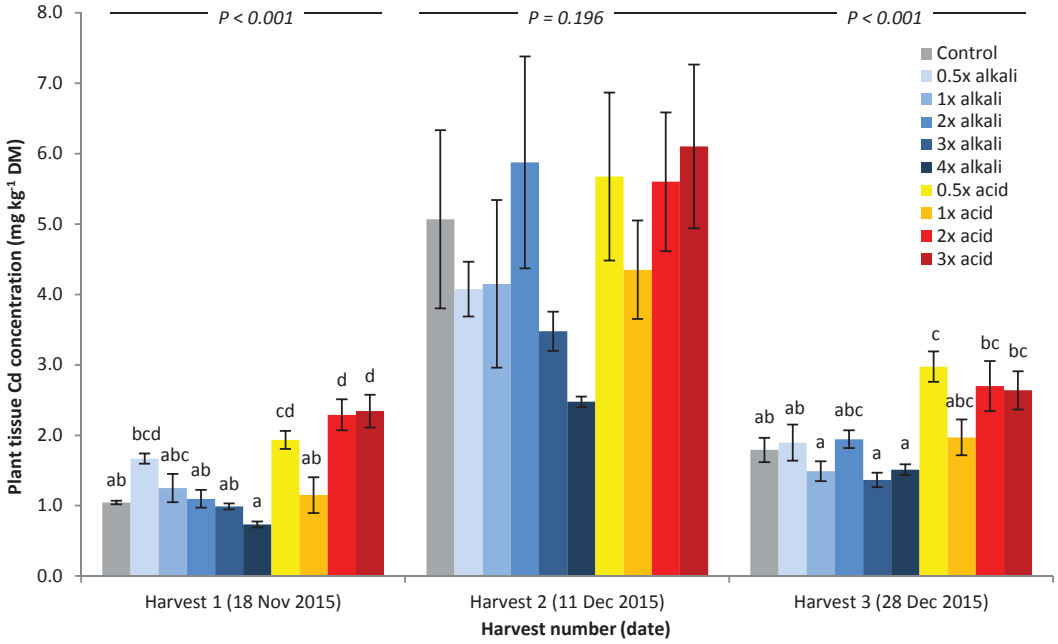

Figure 8.5. Mean chicory Cd concentrations for all alkali/acid treatments within the Topehaehae soil. Error bars represent the standard error. Treatment means within a harvest followed by the same letter are not significantly different from one another ($P < 0.05$).

decrease with increasing rate of hydrated lime in this soil, although only the difference between the lowest and highest rates of hydrated lime (0.5x alkali and 4x alkali) at harvest 1 reached significance ($P < 0.05$). In contrast to the alkali treatments, in both the Kereone and Topehaehae soils, mean tissue Cd concentration for chicory plots amended with ultra-fine elemental sulphur (i.e. acid treatments) were generally greater than those for control plots (the exception being harvest 2 of the Topehaehae soil), although this increase did not always achieve statistical significance ($P < 0.05$) for all treatments.

8.4.2.1.2 Ryegrass

Significant ($P < 0.001$) differences in mean tissue Cd concentration (mg kg^{-1} DM) and mean yield (kg DM ha^{-1}) were also apparent between ryegrass harvests within each soil type (Table 8.7). For both soils, mean ryegrass yield was greatest ($P < 0.05$) at harvest 2, but there was no difference ($P > 0.05$) between yields at harvest 1 and 3. Mean tissue Cd concentration was significantly ($P < 0.05$) lower at harvest 3 relative to harvest 1 and 2. While there was a consistent trend for the greatest mean tissue Cd concentrations at harvest 2 for both soils, these concentrations were not significantly ($P > 0.05$) greater than at harvest 1.

Table 8.7. Ryegrass mean tissue Cd concentration (mg kg^{-1} DM) and mean yield (kg DM ha^{-1}) at each harvest, for both the Kereone and Topehaehae soil types.

Soil type	Ryegrass harvest	Mean tissue Cd conc. (mg kg^{-1} DM)	Mean yield (kg DM ha^{-1})	Mean daily growth rate (kg DM ha^{-1} day^{-1})
Kereone	1	0.152(b)	207(a)	4
	2	0.184(b)	1774(b)	77
	3	0.090(a)	899(b)	53
	P value	*<0.001*	*<0.001*	
Topehaehae	1	0.115(b)	796(a)	15
	2	0.141(b)	2311(b)	100
	3	0.083(a)	574(a)	34
	P value	*<0.001*	*<0.001*	

Treatment-mean ryegrass tissue Cd concentrations for each harvest of the Kereone and Topehaehae sites are presented in Figure 8.6 and Figure 8.7, respectively. Mean ryegrass tissue Cd concentrations at the Kereone site ranged between 0.105-0.271 mg kg^{-1} DM, 0.090-0.443 mg kg^{-1} DM and 0.050-0.142 mg kg^{-1} DM, for the first, second and third harvests. Similar

tissue Cd concentration ranges were seen for the Topehaehae soil, ranging between 0.073-0.171 mg kg^{-1} DM, 0.068-0.215 mg kg^{-1} DM and 0.045-0.133 mg kg^{-1} DM, for the first, second and third harvests, respectively. Within the Kereone soil, alkali/acid treatments only induced a significant ($P < 0.001$) effect on ryegrass tissue Cd concentration at harvest 2 (Figure 8.6). For the Topehaehae soil (Figure 8.7) a significant treatment effect was observed in harvest 2 ($P = 0.007$) and harvest 3 ($P = 0.004$).

Similar to chicory, there was a suggestion that ryegrass tissue Cd concentration had increased with the application of hydrated lime, relative to the control. However, this only reached significance ($P < 0.05$) on one occasion ('3x alkali' treatment at harvest 2 of the Topehaehae soil (Figure 8.7)). Isolated to just the rate of hydrated lime treatments, with the exception of harvest 1 at the Kereone site, there appeared to be a general trend for a decrease in ryegrass tissue Cd concentrations with increasing rate of hydrated lime, although no treatments were significantly different ($P > 0.05$).

In each of the three ryegrass harvests where significant overall treatment effects were observed, there was a trend for mean tissue Cd concentrations to be greater in plots amended with ultra-fine elemental sulphur relative to the controls. However, only the '2x acid' and '3x acid' treatments were greater ($P < 0.05$) than the control at harvest 2 of the Kereone site (Figure 8.6). Within the Topehaehae site (Figure 8.7), only the '2x acid' treatment was greater ($P < 0.05$) than the control at harvest 2, while only the '3x acid' treatment was greater ($P < 0.05$) than the control at harvest 3.

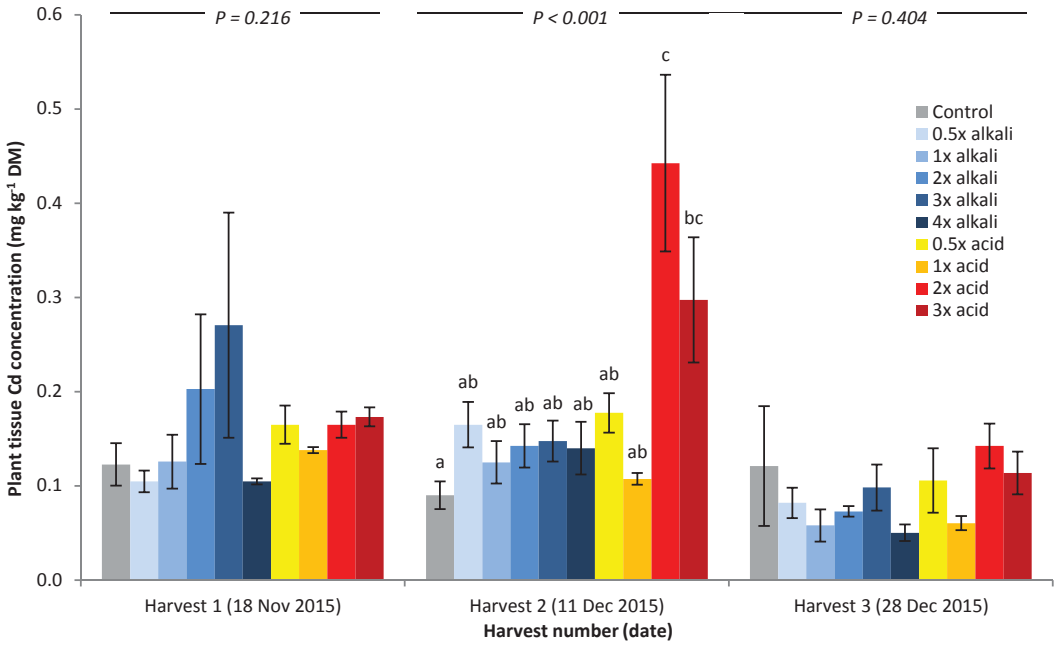

Figure 8.6. Mean ryegrass Cd concentrations for all alkali/acid treatments within the Kereone soil. Error bars represent the standard error. Treatment means within a harvest followed by the same letter are not significantly different from one another ($P < 0.05$).

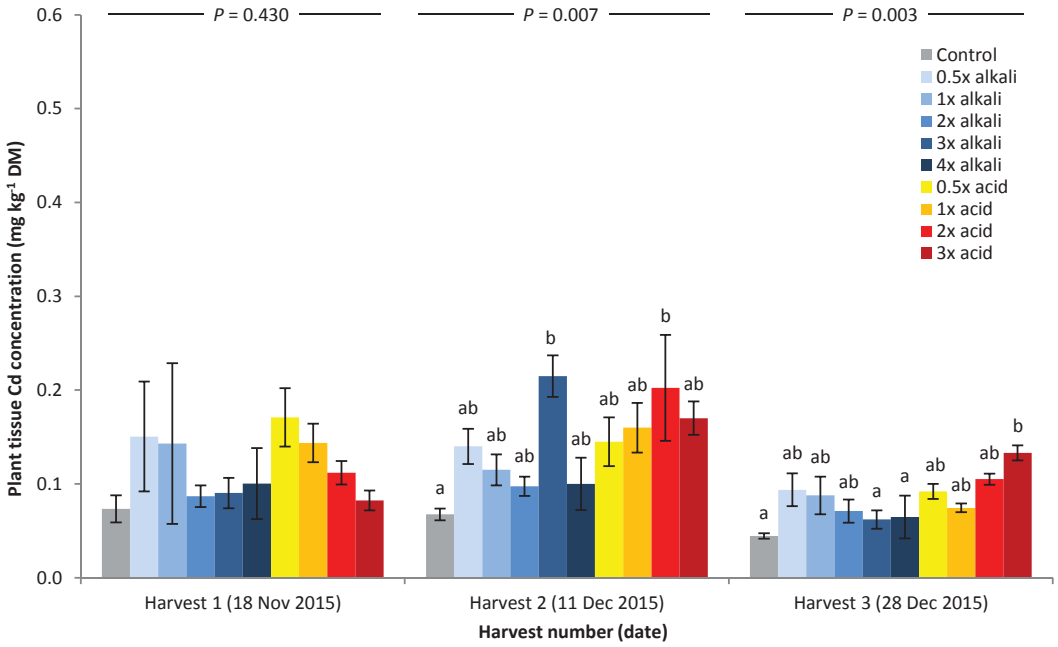

Figure 8.7. Mean ryegrass Cd concentrations for all alkali/acid treatments within the Topehaehae soil. Error bars represent the standard error. Treatment means within a harvest followed by the same letter are not significantly different from one another ($P < 0.05$).

8.4.3 Relationship between soil extractable Cd concentration and pH

Based on the significant ($P < 0.001$) difference in soil extractable Cd concentration between soil types (Table 8.3) the relationship between soil pH and soil extractable Cd concentration was described for individual soil types (Figure 8.8). This analysis showed that there was a significant ($P < 0.001$) negative linear correlation between soil extractable Cd concentration and soil pH, although this relationship was tighter for the Kereone soil ($R^2 = 0.82$) than the Topehaehae soil ($R^2 = 0.64$). The change in extractable Cd concentration per unit increase or decrease 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 8.8) is consistent with the greater total Cd concentration of the Kereone soil (Table 8.1).

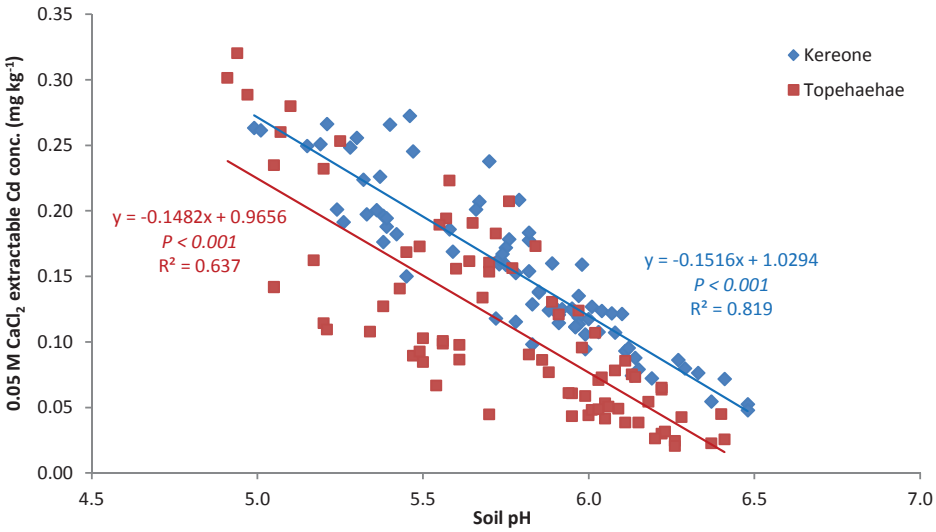

Figure 8.8. Relationship between soil extractable Cd concentration and soil pH for the Kereone and Topehaehae soil types.

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

8.4.4.1 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 8.9.a and Figure 8.9.b, respectively.

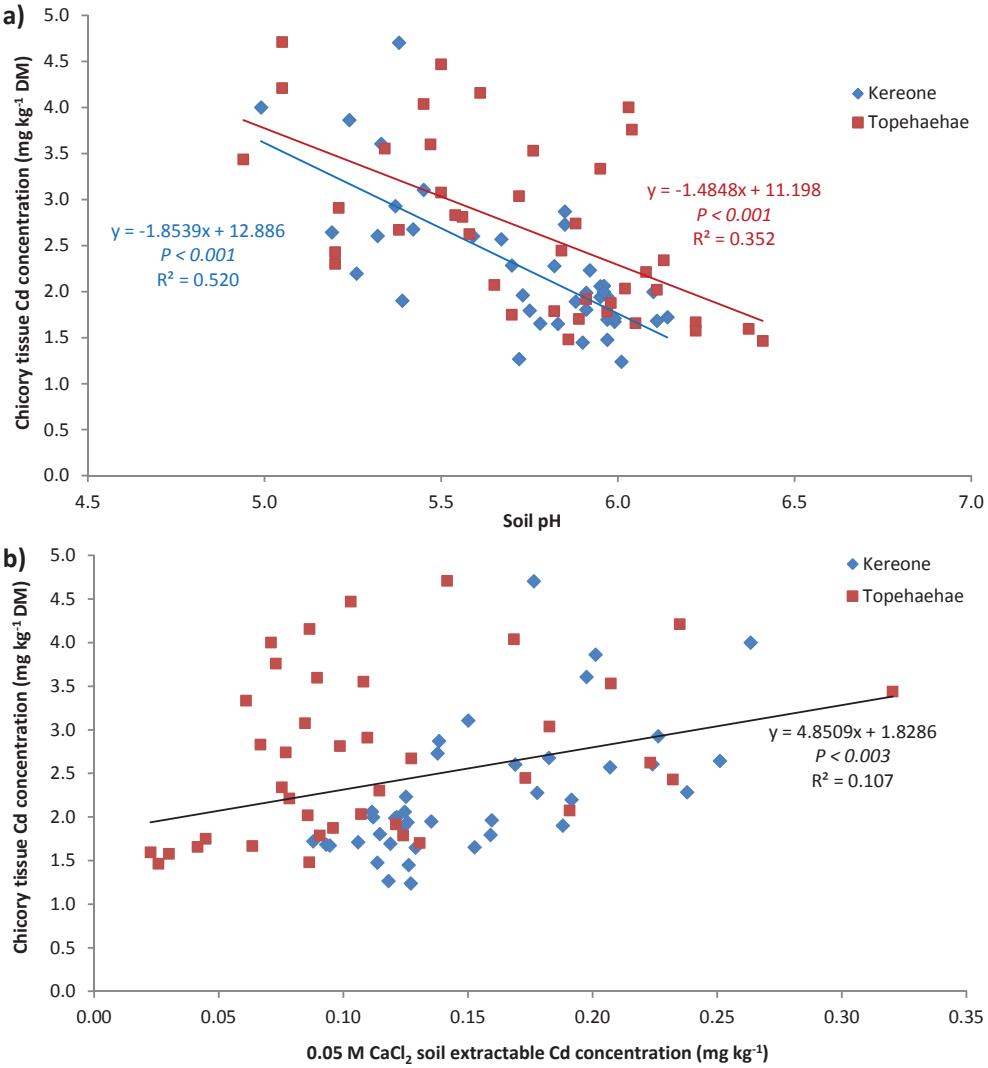

Figure 8.9. Relationship between chicory tissue Cd concentration and **a)** soil pH for the Kereone and Topehaehae soils independently, and **b)** soil extractable Cd concentration across the Kereone and Topehaehae soils combined.

Tissue Cd concentration decreased with increasing soil pH (Figure 8.9.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 8.8. Although chicory tissue Cd concentration (across both soils combined) was positively correlated to soil extractable Cd concentration (Figure 8.9.b) the coefficient of determination was very poor (R^2 = 0.11).

8.4.4.2 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 8.10.a and Figure 8.10.b, respectively. Similar to chicory, ryegrass Cd concentration decreased with increasing soil pH (Figure 8.10.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 8.10.b), however the correlation was very weak (R^2 = 0.28).

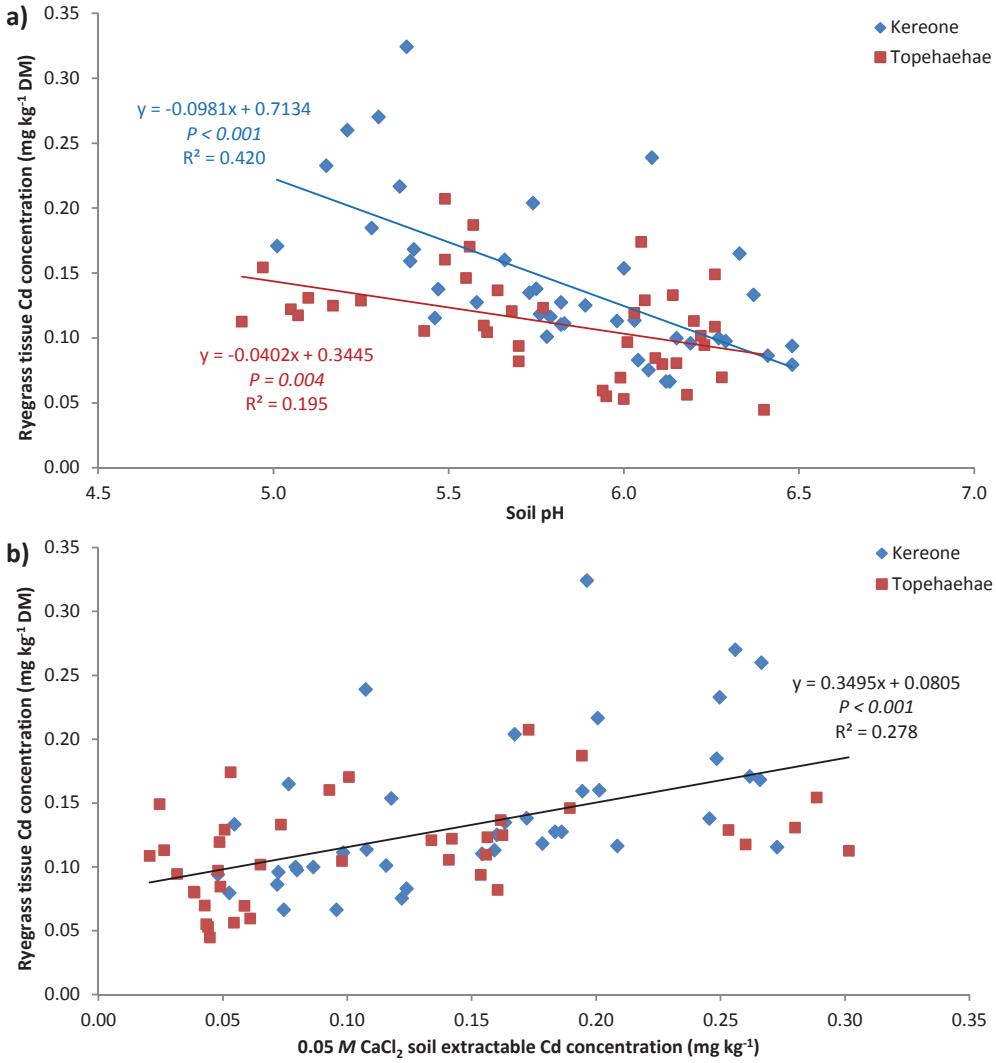

Figure 8.10. Relationship between ryegrass tissue Cd concentration and **a)** soil pH for the Kereone and Topehaehae soils independently, and **b)** soil extractable Cd concentration across the Kereone and Topehaehae soils combined.

8.5 Discussion

8.5.1 Effectiveness of hydrated lime and elemental sulphur treatments

8.5.1.1 Soil pH

Although the effect of elemental sulphur and hydrated lime treatments appeared highly variable (Table 8.4 and Table 8.5) this was assessed further by analysing the main effect of these acid/alkali treatments on soil pH (i.e. across plant species) within each soil (Kereone;

Figure 8.11.a, and Topehaehae; Figure 8.11.b). This analysis confirms significant ($P < 0.001$) differences exists across the various treatments, and that hydrated lime treatments had a smaller influence on increasing soil pH than the ultra-fine elemental sulphur treatments had on decreasing soil pH.

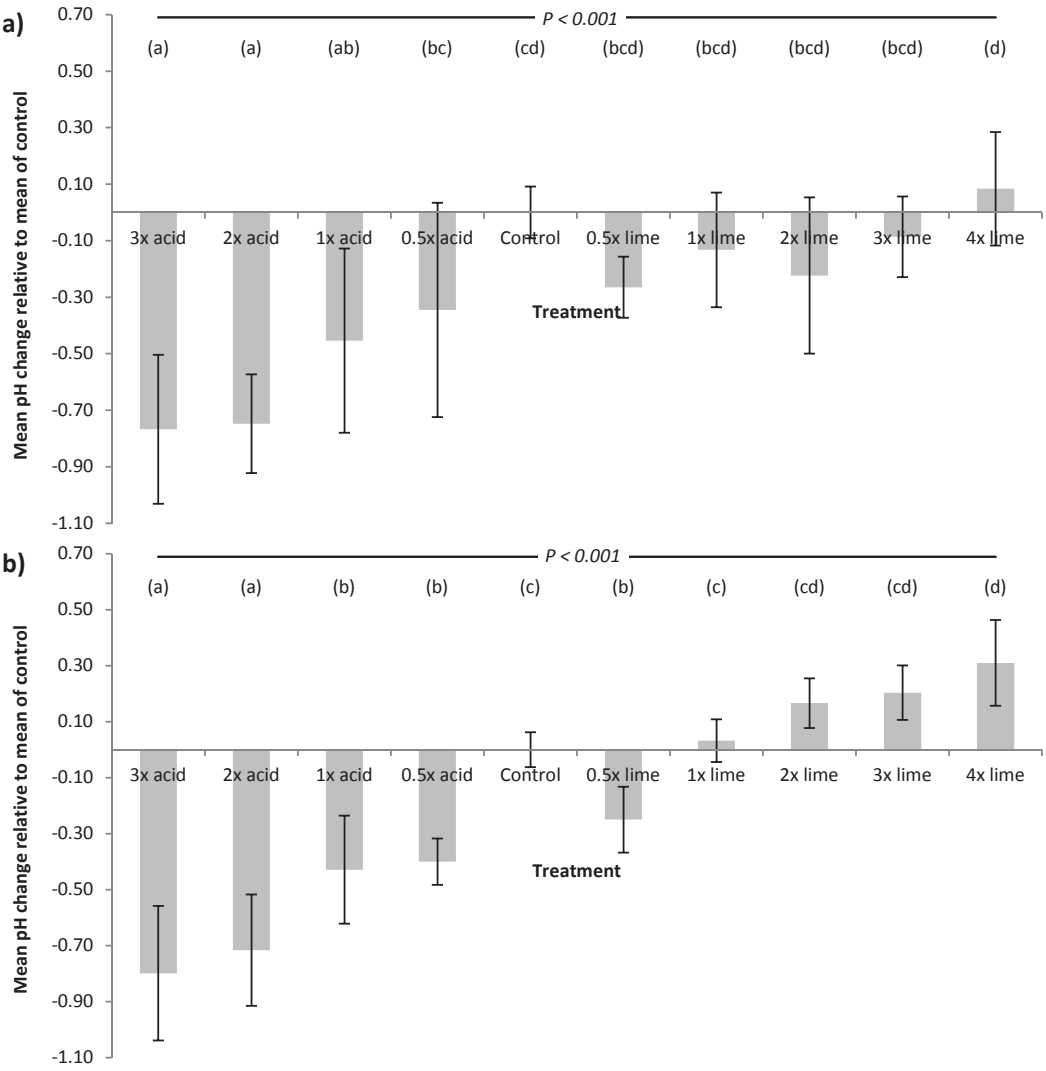

Figure 8.11. Mean change in soil pH for each acid/alkali treatment replicate relative to the mean pH of control, assessed across plant species within each site (n = 8 for each treatment). **a)** Kereone soil, and **b)** Topehaehae soil. Error bars represent the standard deviation. Means with the same letter indicate differences are not significant ($P < 0.05$).

The effectiveness of the ultra-fine elemental sulphur soil amendments in reducing soil pH is consistent with the elemental sulphur oxidation model of Watkinson and Lee (1994). Using this

model, it was calculated that more than 90% of the applied elemental sulphur would have been oxidised within 20 days, given the fine elemental sulphur particle size, and the warm, moist soil at the trial location. This rapid sulphur oxidation is supported by differences in soil pH and corresponding soil extractable Cd concentration for soil samples representing the 'control' and '3x acid' treatments that were taken mid-way through the trial (Appendix 3, Figure A3.1).

Fewer treatments generated significant ($P < 0.05$) changes in pH within the Kereone soil (Figure 8.11.a) than the Topehaehae soil (Figure 8.11.b), reflecting the stronger pH buffering capacity of the Kereone soil (Table 8.1). For example, only the highest rate of hydrated lime (4x alkali) in the Topehaehae soil (Figure 8.11.b) generated a significant ($P < 0.05$) increase in pH above the control, and in this case the treatment mean pH increase (0.31 pH unit) was less than the targeted increase of 0.5 pH unit. Similarly, although an unexpected decrease in soil pH (relative to the control) was recorded for the lowest rate of hydrated lime (0.5x alkali) in both soils, this only reached significance ($P < 0.05$) for the Topehaehae soil (Figure 8.11.b). It is uncertain why this pH decrease occurred. Increased soil solution Ca^{2+} concentrations could potentially increase H^+ exchange into soil solution, but this should only maintain the existing pH equilibrium since equivalent H^+ will have been removed via neutralisation with the introduced OH^-. Potentially, the pH decrease could be explained by greater plant uptake of Ca^{2+} that would increase root efflux of H^+ (Hinsinger *et al.*, 2003). At low rates of hydrated lime this could drive overall acidification, given the soils ability to buffer the pH increase from the small amount of OH^- introduced.

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.*, 1999c; Bolan *et al.*, 2003c) 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.*, 1993a; 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 (Appendix 2, Table A2.1 and Table A2.2). The pH buffer curves developed for these soils (Appendix 2, Figure A2.1 and Figure A2.2) did not indicate stronger pH buffering effects above pH 6.0, which could otherwise have explained the smaller effect on pH from hydrated lime treatments relative to elemental sulphur treatments. 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).

8.5.1.2 Soil extractable Cd and plant tissue Cd concentrations

Large variability in soil extractable Cd concentrations and plant tissue Cd concentration meant that significant ($P < 0.05$) differences between individual hydrated lime or elemental sulphur treatments were not always detectable (Table 8.4 and Table 8.5). In particular, this was the case for ryegrass. This was likely due to the lower tissue Cd concentrations, smaller change in tissue Cd concentrations per unit change in soil pH, and weaker correlation between tissue Cd concentration and soil pH (Figure 8.10.a) relative to chicory (Figure 8.9.a). Although treatment effects were also variable for chicory, for this species there was a consistent trend for greater mean tissue Cd concentrations in elemental sulphur treatments relative to the controls in both soils (Table 8.4 and Table 8.5), although these only reached significance for the '1x acid' and '2x acid' treatments in the Kereone soil (Table 8.4). Within individual harvests, chicory tissue Cd concentrations in elemental sulphur treatments were also significantly ($P < 0.05$) greater than the control at harvests 1 and 3 (Figure 8.4 and Figure 8.5).

The non-significant trend for an increase in plant tissue Cd concentration under the low rate of hydrated lime treatments compared to control plots for both plant species in both soil types (Figure 8.4, Figure 8.5, Figure 8.6 and Figure 8.7) was an unexpected observation. There are several possible explanations for this effect. Firstly, these low rates of hydrated lime were not expected to drive large increases in soil pH, and concurrently, Cd sorption. Without a large increase in Cd sorption, it is possible that a rapid increase in soil solution Ca^{2+} concentrations following dissolution of hydrated lime may have increased Cd^{2+} desorption and phytoavailability through competitive ion exchange (John *et al.*, 1972; Williams and David, 1976; Christensen, 1984; Boekhold *et al.*, 1993; Naidu *et al.*, 1994; Bolan *et al.*, 2003c). This is consistent with the significant ($P < 0.05$) increase in soil extractable Cd concentration observed for the lowest rate of hydrated lime (0.5x alkali) in ryegrass replicates of the Kereone soil (Table 8.4) and replicates of both plant species in the Topehaehae soil (Table 8.5). Increased root vigour and greater root exploration has also been cited as a possible reason for unexpected increases in plant tissue Cd concentration following liming (Gray *et al.*, 1999c). In addition, as previously discussed, increased plant Ca^{2+} uptake will cause greater root efflux of H^+ (Hinsinger *et al.*, 2003), thereby increasing soil Cd desorption and plant Cd uptake.

With the large variability within and between treatments, the regressions (using individual replicate data values) between soil pH and soil extractable Cd concentration, and between soil pH or extractable Cd concentration and plant tissue Cd concentration, provide a better insight into the effect of alkali/acid treatments on soil Cd phytoavailability and plant Cd accumulation. In particular, this is shown by the significant ($P < 0.001$) negative linear correlation between soil pH and soil extractable Cd concentration (Figure 8.8). This relationship should be expected across the relatively narrow pH range generated, given that Cd sorption and solubility is heavily influenced by pH in variable charge soils, with specific sorption capacity increasing and Cd solubility decreasing as soil pH increases (Tiller *et al.*, 1984; Naidu *et al.*, 1994; Bolan *et al.*, 2003c; Srivastava *et al.*, 2005).

Unfortunately, the relationship between plant tissue Cd concentration and soil pH or soil extractable Cd concentration (Figure 8.9 and Figure 8.10) 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).

The poor correlation between 0.05 M $CaCl_2$ extractable soil Cd and plant tissue Cd concentrations overall (Figure 8.9.b and Figure 8.10.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, c; 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, c). 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.*, 1994b; Gray *et al.*, 1999c).

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, c), 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, c). 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, c; 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, c). Given the focus on manipulation of soil pH on soil Cd phytoavailability in this study, this was considered a critical characteristic.

8.5.2 Prediction of chicory tissue Cd concentration based on total Cd total C, and pH

Although soil extractable Cd concentration showed little use in predicting tissue Cd concentration for chicory (R^2 = 0.11; Figure 8.9.b) or ryegrass (R^2 = 0.28, Figure 8.10.b), previous research within this thesis reported that 75% of the variability in chicory tissue Cd concentrations could be explained by the variables soil total Cd, total C and pH (Chapter 5, Table 5.5). Using total Cd and total C data for the two soils in this trial (Table 8.1) and the pH

data for the individual replicates, chicory tissue Cd concentration was predicted using the regression equation derived from the field survey (Chapter 5, Table 5.5) and plotted against actual tissue Cd concentration (Figure 8.12). A significant (P = 0.001) relationship existed between predicted and actual tissue Cd concentrations, although only 14% of the variability in tissue Cd concentrations could be explained, considerably less than the coefficient of determination achieved within the field survey (R^2 = 0.75). In addition, the slope of the 'best-fit' relationship deviated substantially from the 1:1 line. This indicates that the chicory tissue Cd concentration predictive model developed from the original field survey dataset (Chapter 5) was not sufficiently robust when applied to the two soils manipulated with acid/alkali treatments within this field trial.

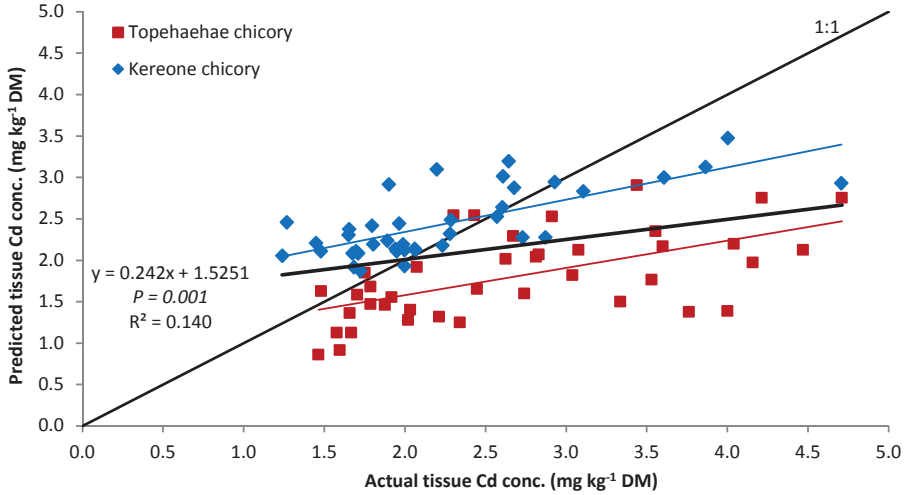

Figure 8.12. Relationship between actual chicory tissue Cd concentrations determined for individual replicates in this trial and those predicted using the regression equation from Chapter 5 (*Chicory tissue Cd = 1.828[Soil total Cd] - 1.391[Soil pH] - 0.054[Soil total C] + 8.729)*).

Inability of the predictive model to explain most of the variability in the field trial tissue Cd dataset could be related to the lack of total Cd and total C data at the replicate level. These factors were treated as constants within each soil type, with pH being the only variable that was assessed specific to each replicate. However, as the majority of data points for the Kereone soil were over-predicted and the majority of Topehaehae data points were under-

predicted (Figure 8.12), this suggests that the original model was too sensitive to soil total Cd concentration (much greater for the Kereone soil; Table 8.1) and not sensitive enough to total C concentration (much greater for the Kereone soil; Table 8.1) and soil pH. This is further reinforced by the increased under-prediction of tissue Cd concentrations as actual tissue Cd concentration increased, since chicory tissue Cd concentration was previously shown to be inversely related to soil pH (Figure 8.9.a).

8.5.3 Tissue Cd concentrations over time

Although an inverse relationship between plant yield and plant tissue Cd concentration has been previously cited in the literature (Mortvedt *et al.*, 1981; Loganathan *et al.*, 1997; Gray *et al.*, 1999c; Roberts and Longhurst, 2002) this tissue Cd 'dilution' effect was not evident in the current trial. In contrast, the greatest mean tissue Cd concentrations for chicory occurred during harvest 2 at both sites (Figure 8.4, Figure 8.5 and Table 8.6), coinciding with the greatest mean dry matter yields and mean daily dry matter accumulation rates. For example, tissue Cd concentrations for chicory were approximately 2-3 times greater at harvest 2 than harvest 1, despite growth rates being approximately 4 times greater during the second growth cycle (Table 8.6). Similarly, ryegrass tissue Cd concentrations did not appear to be inversely related to yield / daily growth rate (Table 8.7).

It is possible that the low tissue Cd concentrations at harvest 1 for both plant species could be partly explained by plants having a limited root network over early development, which would limit their exposure to Cd in soil solution and on soil sorption surfaces (Gray *et al.*, 1999c). In addition, gradual soil acidification related to increased mineralisation of soil organic matter and nitrification following cultivation (Ridley *et al.*, 1990; Bolan *et al.*, 1991; McLaren and Cameron, 1996) could also explain the increase in plant tissue Cd concentration at harvest 2. However, neither of these processes can explain the subsequent decrease in plant tissue Cd concentration seen at harvest 3 for both plant species and sites (Table 8.6 and Table 8.7).

Temporary acidification of the soil surrounding fine root hairs resulting from the efflux of H^+ and organic acids can influence soil Cd desorption, solubilisation and uptake (Welch and Shuman, 1995; Welch and Norvell, 1999; Hinsinger *et al.*, 2003). Greater root efflux of H^+ and organic acids as a result of greater plant growth rates during the 2nd growth cycle (Table 8.6 and Table 8.7) would therefore be consistent with the greater tissue Cd concentrations seen at harvest 2. Potentially, the reduction in plant tissue Cd concentrations between harvests 2 and 3 could also be explained by the more labile non-specifically sorbed Cd having already been desorbed and taken up by plant roots during the second growth cycle, with slower subsequent rates of desorption (Gray *et al.*, 1998, 1999d).

Alternatively, differences in soil moisture could also explain differences in plant tissue Cd accumulation between harvests 2 and 3. Rainfall (and consequently soil moisture) over growth cycles 2 and 3 was strongly contrasting. Approximately 14 days prior to harvest 2, the largest rainfall event (23 mm within a 24 hour period; Figure 8.3) of the entire trial duration occurred, which rewet the soil profile. In contrast, there was virtually no rainfall (1 mm; Figure 8.3) between harvests 2 and 3, resulting in an obvious decrease in soil moisture content over this period. As ion diffusion is expected to decrease with decreasing soil moisture (McLaren and Cameron, 1996; Havlin *et al.*, 2005) the increase in soil moisture during the 2nd growth cycle is consistent with the greater plant tissue Cd concentrations at the 2nd harvest.

Previous pot-trial research within this thesis (Chapter 7) indicated that short-term fluctuations in soil moisture can also influence soil extractable Cd concentrations, with increases occurring following increases in soil moisture. The observation of greater plant tissue Cd concentrations at the 2nd harvest following the increase in soil moisture during that growth cycle is therefore consistent with the findings of this earlier pot trial. It is also consistent with the observations of Loganathan *et al.* (1997), who noted that autumn increases in pasture Cd concentration could be a consequence of increased soil Cd sorption and solubility brought about by increases in soil moisture.

Lastly, consistent with previous research (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999) the majority of the Cd in these infrequently-cultivated pastoral soils is located near the soil surface (Chapter 3, Figure 3.18). Hence, with greater moisture in the Cd-enriched topsoil, greater root activity in this soil layer is likely to increase plant Cd uptake and accumulation, relative to drier periods where plants are forced to extract moisture and nutrients from deeper in the soil profile.

8.5.4 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 (Chapter 4, Stafford *et al.* (2016)) and a field survey (Chapter 5). 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 (Chapter 2, Table 2.10). As discussed within Chapter 4 (Section 4.4.6.1) 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, 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 8.8) is consistent with previous research showing Cd solubility / extractable Cd concentration to be negatively correlated to soil pH (He and Singh, 1993b; McBride *et al.*, 1997; Gray *et al.*, 1998, 1999d). However, while tissue Cd concentrations for both chicory (Figure 8.9) and ryegrass (Figure 8.10) 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 8.9.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 8.9.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.* (1999c) 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 (1993b) reported an approximate 40% reduction in Cd concentration in mixed-grass samples at pH of 6.5 compared to 5.5.

To provide context, in the European Union a directive is in place that stipulates that animal feeds of vegetable origin must contain less than 1.136 mg Cd kg^{-1} DM (EC, 2013). Although not currently applicable to New Zealand livestock grazing systems, if such policy was implemented in New Zealand to align with European market / consumer ideals, soil pH would need to be increased to 6.4 and 6.8 (Kereone and Topehaehae soils, respectively) to manage mean chicory tissue Cd concentration to below 1.136 mg kg^{-1} DM (based on the regression equations in Figure 8.9.a). While this is technically feasible, other factors in addition to soil pH manipulation need to be considered with regard to managing Cd accumulation in chicory, given this factor alone only explained a modest proportion (R^2 = 0.35-0.52) of variability in tissue Cd concentrations in this trial. This is consistent with previous research. For example, Sparrow and Salardini (1997) reported that despite managing other variables within a site that can influence Cd accumulation (including cultivar, soil mineralogy and fertiliser inputs), soil pH alone could only explain 22% of the variability in potato tuber Cd concentrations. These authors also noted that the decrease in tissue Cd concentrations from increasing pH was smaller than the

variability in crop tissue Cd concentration between years, similar to the findings in cereals of Oliver *et al.* (1996).

Evidence from this trial supports previous work (Chapter 7) that indicates soil moisture is an important factor that influences plant tissue Cd accumulation in the presence of Cd-enriched topsoil. Although soil moisture cannot be managed in New Zealand's predominantly rain-fed grazed pasture systems, tillage management to reduce topsoil Cd concentrations stands out as an important strategy to decrease overall soil Cd phytoavailability, as well as to manage increases in Cd phytoavailability that occur with increases in soil moisture. Furthermore, plant breeding opportunities to reduce Cd accumulation in vegetative tissue of Cd-accumulating species such as chicory should be explored.

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. Similarly, an algorithm developed from a previous field survey to explain chicory tissue Cd concentrations based on the variables soil total Cd, total C and pH was not successful when applied to the dataset in this trial. Sensitivity and reliability of this model may have been limited by the absence of replicate-specific measurements of total Cd and total C. It is also possible that the abrupt changes to pH and Cd solubility brought about by the application of elemental sulphur, and to a lesser extent hydrated lime, are not well handled by this model, which is based on relationships derived from a range of soils without an 'artificial' influence imposed on the background soil pH.

8.6 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 to ryegrass, chicory tissue Cd concentrations were highly variable between harvests (~1.0-6.0 mg kg^{-1} DM), with the greatest tissue Cd concentrations coinciding with a period of increased soil moisture, supporting previous pot trial findings. Regression analysis of chicory tissue Cd concentration and soil pH data indicated a mean decrease in tissue Cd concentration of approximately 1.5-1.9 mg kg^{-1} DM per unit pH change. 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.

CHAPTER 9 : Integrated discussion - key research findings, implications and suggestions for future research

9.1 Introduction

Managing soil Cd accumulation is a desirable strategic objective for New Zealand agriculture. The implementation of the TFMS in 2011 (MAF, 2011) has put in place a structure that's has potential to manage on-going soil Cd accumulation. Further to this, conversion of agricultural land to alternative land use (e.g. rural-residential dwellings) now prompts contaminated land assessment under the NES (MfE, 2011), which has potential to affect land use flexibility. The implementation of the TFMS and NES has therefore increased awareness of soil Cd enrichment, and in doing so, has also raised questions regarding within-farm soil Cd variability, and appropriate soil sampling methodology. In particular, this is the case for properties that have had a rich P fertiliser history and consequently greater soil Cd concentrations, such as traditional dairy farming land on Allophanic, Pumice and Organic soil orders in the Waikato, Bay of Plenty and Taranaki regions (Roberts *et al.*, 1994; Taylor *et al.*, 2007; Cavanagh, 2014b).

Managing soil Cd accumulation in these agricultural systems is, however, only part of the issue. Provided that soil biological function / productive capacity is not impaired, then the primary objective should be in managing plant tissue Cd accumulation, since livestock Cd accumulation (mainly in the liver and kidney) is directly related to daily total dietary Cd intake (Lee *et al.*, 1994; Lee *et al.*, 1996). Most historic research on plant tissue Cd accumulation in New Zealand agriculture has focussed on ryegrass and white clover, the traditional backbone of New Zealand's grazed pasture systems, which do not accumulate high Cd concentrations in above-ground vegetative tissue (Roberts *et al.*, 1994; Loganathan *et al.*, 1997; Reiser *et al.*, 2014). However, over the last 10-20 years, there has been significant diversification of the forage

species used either as monocultures or within diverse pasture mixes. In particular, chicory and plantain are now commonly used as specialist livestock forage crops due to the greater feed quality and production of these species, relative to ryegrass and white clover, over the dry summer months (Somasiri *et al.*, 2015). Currently, there is little knowledge pertaining to Cd accumulation in these crops and consequent risk of Cd transfer to grazing livestock (Reiser *et al.*, 2014). In addition, there has been little assessment of factors known to influence soil Cd phytoavailability (e.g. soil pH modification (Gray *et al.*, 1999c)) under field conditions for New Zealand soils and livestock forage species.

Therefore, from an initial review of the existing literature, the following key knowledge gaps were identified:

- How do soil total Cd concentrations vary spatially and within the soil profile in long-term dairy farms, taking into account differences in management history, soil type, tillage practices, etc.?
- What is the relative Cd accumulation potential of different forage species used in modern livestock grazing systems New Zealand, and how does this influence the risk of Cd accumulation in grazing livestock?
- How is soil Cd phytoavailability influenced by fluctuation in soil moisture content?
- How much influence does manipulation of soil pH have on soil Cd phytoavailability and plant tissue Cd accumulation?

9.2 Key research findings

9.2.1 Soil total Cd concentrations are highly variable in the soil profile and across paddocks

All paddock testing (Chapter 3) was carried out in two long-term dairy farms (Waikato and Canterbury regions) with contrasting management history and soil types. Soil total Cd concentration (0-150 mm depth) ranged between 0.48-1.64 mg kg^{-1} and 0.15-0.64 mg kg^{-1}

within the Waikato and Canterbury farms, respectively. As indicated by the strong positive linear correlation ($P < 0.001$, $R^2 = 0.84$-0.85) between soil total P and total Cd, differences in P fertiliser application history was the dominant factor influencing variation in soil total Cd concentrations between properties, and also between blocks within a property.

Within blocks of common P fertiliser management history, there was a significant ($P < 0.001$) effect of soil type on soil total Cd concentration. Within the Waikato property, total Cd concentrations were significantly greater in the Kereone (Allophanic) soils than the Topehaehae / Topehaehae (Gley) soils. Within the original dairy block of the Canterbury property, total Cd concentrations descended in the order Waimairi (Peaty Loam) > Temuka (Gley) > Wakanui (Pallic). Despite uniform P fertiliser application within these properties, the greatest soil total Cd concentrations were found in soils with greatest Cd-sorption potential, with strong correlation between total Cd and total C (Spearman's *rho* = 0.726-0.864) or total N (*rho* = 0.742-0.840) in both properties.

In contrast to P fertiliser management history and soil type, slope had little influence on Cd accumulation, only influencing soil total Cd concentration when gradient was greater than 15°. Effluent application had no detectable effect on Cd accumulation. Calculations made on the proportion of dung deposited in the dairy shed suggested that where that rate of P fertiliser application was reduced in effluent blocks in recognition of the P applied in effluent, the total amount of Cd applied in effluent and P fertiliser would be less than that applied to corresponding blocks receiving only P fertiliser.

Soil Cd concentrations were non-uniformly distributed within the soil profile of both properties. The mean soil Cd concentration at a sampling depth of 0-150 mm represented 94% and 82% of that assessed at 0-75 mm, for the Canterbury and Waikato farms, respectively. However, total Cd concentration in soils of the Waikato property showed a stronger, more consistent decline with depth relative to those in the Canterbury property, where soil Cd

concentrations were relatively uniform over a depth range of 0-200 mm, before declining thereafter. This reflects differences in tillage history between the two properties, with a 'no-tillage' pasture-only management philosophy being employed in the Waikato property, versus a history of rotational cropping and/or pasture renewal within the Canterbury property.

Even with P fertiliser management history, soil type and sampling depth taken into account, there was a large degree of soil Cd variability within paddocks of common land management units, within both properties. To obtain the most robust appraisal of soil Cd concentration (particularly where critical soil Cd concentration values are being approached) it is therefore recommended that all paddocks / soil types are sampled within each land management unit, such that an area-weighted average soil Cd concentration can be determined for the property. Consistent with the recommendations of FANZ (2016), sampling should be undertaken at 0-150 mm depth to better account for differences in soil tillage history between properties.

9.2.2 Cadmium concentrations in chicory and plantain were several fold higher than ryegrass and white clover

An initial pot trial (Chapter 4) revealed that large variation in plant tissue Cd concentration exists within various forage plant species commonly used in New Zealand livestock grazing systems. Tissue Cd concentrations in chicory and plantain were particularly enriched (1.639 and 0.734 mg kg^{-1} DM, respectively) relative to ryegrass and white clover (0.103 and 0.035 mg kg^{-1} DM, respectively).

A subsequent field survey (Chapter 5) carried out on commercial farms on different soil types and land use histories throughout New Zealand validated the findings of the pot trial, with mean tissue Cd concentrations decreasing in the order chicory (1.820 mg kg^{-1} DM) > plantain (0.803 mg kg^{-1} DM) > ryegrass (0.114 mg kg^{-1} DM) > white clover (0.074 mg kg^{-1} DM). Wide tissue Cd concentration ranges for chicory (0.40-4.50 mg kg^{-1} DM) and plantain (0.23-2.40 mg kg^{-1} DM) indicated the sensitivity of these species to soil Cd phytoavailability, relative to

ryegrass and white clover where all samples were less than <0.3 mg kg^{-1} DM. However, only the tissue Cd concentration of chicory could be satisfactorily explained by the soil variables total Cd, total C, and pH (R^2 = 0.745), with soil total Cd being the dominant variable (R^2 = 0.55 for total Cd alone).

Animal accumulation risk modelling indicated that grazing chicory or plantain crops as a high percentage of the diet could result in rapid accumulation of Cd in the liver and/or kidney of grazing livestock, potentially resulting in animal offal exceeding domestic or international food standards well in advance of the current meat industry animal offal discard age (30 months).

9.2.3 Fluctuating soil moisture has only a minor effect on Cd solubility, but increased soil moisture may still increase plant Cd uptake

A pot trial (Chapter 7) was established to evaluate the effect of fluctuating soil moisture and only short-term (3-day) periods of soil saturation on soil Cd phytoavailability and Cd accumulation in plantain, on two different soil types (Kereone [Allophanic], total Cd 0.79 mg kg^{-1}; and Topehaehae [Gley], total Cd 0.61 mg kg^{-1}). Overall, this trial showed that there was no difference in soil extractable Cd concentration or plant tissue Cd accumulation under contrasting 'flooded' (3 days flooded and then 11 days drained) and 'non-flooded' (irrigation to 70% of potted field capacity every 7 days with continuous drainage) irrigation regimes. However, regardless of irrigation regime, there was a trend for an increase in soil extractable Cd concentration with an increase in soil moisture following periods of soil drainage / drying. Coupled with increased rate of ion-diffusion at greater soil moisture content (McLaren and Cameron, 1996; Havlin *et al.*, 2005) these factors may result in greater root Cd^{2+} absorption and plant tissue Cd accumulation with increased soil moisture. Although timing of grazing cannot be managed around rainfall events in a non-irrigated, grazed pastoral system, irrigation input and timing relative to harvest schedules could be an important management factor for reducing Cd accumulation in Cd-sensitive horticultural food crops.

This trial also demonstrated the importance of taking into account soil organic matter and pH when assessing Cd phytoavailability risk. Despite the greater soil total Cd concentration of the Kereone soil, both soil extractable Cd concentration and plant tissue Cd accumulation were significantly ($P < 0.05$) greater for the Topehaehae soil (325% and 183%, respectively), reflecting its much lower pH and organic matter content. Relative Cd solubility for the two soils was successfully predicted by the soil variables total Cd, organic matter and pH, using the equation of Gray *et al.* (1999d).

9.2.4 There is long-term risk of increased soil Cd bioavailability if soil pH declines

Two field trials (Chapter 8) were established on contrasting soils (Kereone [Allophanic], total Cd 1.12 mg kg^{-1}, pH 6.1; and Topehaehae [Gley], total Cd 0.67 mg kg^{-1}, pH 6.1) to evaluate the influence of pH manipulation (using ultra-fine elemental sulphur and hydrated lime soil amendments) on soil Cd phytoavailability and Cd accumulation in chicory and perennial ryegrass.

Overall, mean tissue Cd concentrations (control plot data only) were significantly ($P < 0.001$) greater for chicory (1.643-2.413 mg kg^{-1} DM, respectively) than ryegrass (0.062-0.111 mg kg^{-1} DM, respectively), further validating previous glasshouse (Chapter 4) and field survey (Chapter 5) findings. Ultra-fine elemental sulphur and hydrated lime treatments were effective in generating a large pH range (approximately 5.0-6.5) in both soils, although the effects of individual treatments were variable, and generally smaller for the Kereone soil due to its greater pH buffering capacity. Soil extractable Cd concentration decreased linearly with increasing soil pH in both the Kereone and Topehaehae soils (R^2 = 0.64 and 0.82, respectively). Plant tissue Cd concentration decreased with increasing pH, with a greater proportion of the variability in tissue Cd concentration explained for chicory (R^2 = 0.35-0.52) than ryegrass (R^2 = 0.19-0.42). Correspondingly, plant tissue Cd concentrations increased with increasing soil extractable Cd concentration. However, 0.05 M $CaCl_2$ extractable Cd concentration was only

able to explain 11% and 28% of the variability in chicory and ryegrass Cd concentrations when applied across soil types. This suggests that this extractant is not a reliable indicator of Cd phytoavailability (for either ryegrass or chicory) following recent application of alkali / acid amendments to modify soil pH and Cd sorption behaviour. Application of an algorithm previously developed from a field survey (Chapter 5) to predict chicory Cd concentration based on soil total Cd, total C and pH, was also unsuccessful (R^2 = 0.14) in predicting chicory tissue Cd concentration. The ability of this model is likely to have been limited by the lack of replicate-specific total Cd and total C concentration data. However, overall it did not appear sensitive enough to differences imposed by pH modifications, as well as differences in soil total C between soils at this site, and consequently appeared too sensitive to differences in total Cd.

Mean tissue Cd concentrations in chicory varied greatly between the three harvests. Contradicting the inverse relationship that is commonly reported between plant growth rate and tissue Cd concentration (Mortvedt *et al.*, 1981; Loganathan *et al.*, 1997) tissue Cd concentrations of chicory were greatest ($P < 0.05$) at the 2nd harvest, following the greatest growth rates that occurred in that growth cycle. The greater tissue Cd concentrations and yields at the second harvest coincided with a large rainfall event that occurred midway through the 2nd growth cycle. In contrast, the lower tissue Cd concentrations and yields at the 1st and 3rd harvests aligned with periods where the soils were relatively dry as a consequence of light, infrequent rainfall. These findings therefore appeared consistent with the previously-discussed findings of the 'soil moisture' pot trial (Chapter 7) as well as the base principle of increased ion-diffusion with increased soil moisture.

Ryegrass tissue Cd concentrations remained low (generally <0.3 mg kg^{-1} DM) even at a soil pH of ~5.0. In contrast, regression data for chicory indicated a mean tissue Cd concentration of approximately 4.0 mg kg^{-1} DM at a soil pH of 5.0, which decreased by approximately 1.5-1.9 mg kg^{-1} DM per unit pH change. These findings suggest that for ryegrass-dominant pasture, there is little justification for increasing soil pH beyond the agronomic optimum of 5.8-6.0 (Roberts

and Morton, 2009)) to reduce plant tissue Cd accumulation, since there is little risk of increased animal Cd accumulation at low soil pH. However, for chicory as a 'Cd-accumulating' plant species, increasing soil pH to a minimum of 6.5 is a practical means of decreasing tissue Cd accumulation in chicory and risk of livestock dietary Cd exposure. Conversely, the sensitivity of chicory tissue Cd concentrations to soil pH also highlights the potential risk to increased livestock dietary Cd exposure through gradual soil acidification, which is likely to occur in high yielding chicory forage stands when lime is under-applied.

9.2.5 NIRS is a promising technique for rapid, low cost assessment of soil management history and the relative distribution of Cd in the soil profile

Visible and near-infrared reflectance spectroscopy (NIRS) was able to successfully predict soil total C (R^2 = 0.91-0.95, RMSECV(%) = 0.40-0.64, RPD = 3.41-4.33) and total N concentrations (R^2 = 0.91-0.92, RMSECV(%) = 0.04-0.08, RPD = 3.43-3.57) within the soil profiles of both properties (Chapter 6). Furthermore, due to the strong correlation (R^2 = 0.83-0.90) between total Cd and soil total C or total N within individual properties (peaty loam soils of the Canterbury farm excluded), NIRS analysis also showed promise for use in predicting the relative distribution of Cd in the soil profile. Prediction of absolute soil Cd concentrations at different sites will, however, be complicated by variation in soil Cd:C (or Cd:N) ratios that are driven by differences in soil type and/or P fertiliser management history.

NIRS therefore offers potential as a rapid, low cost analytical technique for assessing soil tillage history, and the consequent impact this has had on the redistribution of Cd in the soil profile. This information is particularly important when assessing remediation options to reduce soil total Cd concentration to a desired target, for example, the tillage depth that is required to reduce soil total Cd concentration to less than the NES soil contaminant standard for rural residential land use of 0.8 mg kg^{-1} (discussed subsequently in Section 9.3.2.3).

9.3 Implications of this research for Cd management

9.3.1 Animal Cd accumulation

As Cd accumulation in the liver and kidney of grazing livestock is known to increase with increasing dietary Cd intake (Lee *et al.*, 1994; Lee *et al.*, 1996) this research reinforces the importance of accounting for different plant species when assessing risk of animal Cd accumulation. This is exemplified by the tissue Cd concentrations determined for chicory (0.5-5.0 mg kg^{-1} DM), which were approximately an order of magnitude greater than those of ryegrass and white clover pasture (0.02-0.30 mg kg^{-1} DM). Hence, risk of animal Cd accumulation could be greater when grazing Cd-accumulating plant species such as chicory and plantain even in relatively low Cd soils, whereas tissue Cd concentrations in ryegrass and white clover remained low (<0.3 mg kg^{-1} DM) regardless of soil total Cd concentration.

As the difference in chicory and ryegrass tissue Cd accumulation was evident even at relatively low soil Cd concentrations (e.g. within 'tier 0' of the TFMS (<0.6 mg kg^{-1} soil)) managing soil Cd accumulation will not be sufficient for managing potential risks related to elevated animal dietary Cd intake when grazing these Cd-accumulating crops. An opportunity to manage Cd accumulation in Cd-sensitive plant species such as chicory may therefore lie in plant breeding initiatives to develop cultivars selected for decreased Cd accumulation in their vegetative tissue. This approach has already been successfully used to decrease Cd accumulation in the edible tissues of numerous food crops, including sunflower, rice, durum wheat and soybean (Li *et al.*, 1997; Liu *et al.*, 2007; Grant *et al.*, 2008).

9.3.2 Remediating high Cd soils

9.3.2.1 Phytoremediation

As an alternative to selective plant breeding to decrease Cd accumulation in chicory, potentially this crop could be used for phytoremediation purposes if cultivars could be

developed with greater capacity for Cd accumulation in the vegetative tissues. Field evidence in this research suggested that chicory tissue Cd concentrations were generally greater than 1 mg kg^{-1} and could approach 4-6 mg kg^{-1} DM with favourable soil conditions (e.g. soil total Cd > 1 mg kg^{-1}, soil pH < 5.5). In a cut and carry system, assuming a yield of 15 t DM ha^{-1} y^{-1}, a mean tissue Cd concentration of 5 mg kg^{-1} DM, and a soil bulk density of 0.8 t m^{-3}, in theory should take 8 years to decrease soil Cd concentrations by 0.5 mg kg^{-1}. This assumes that the soil is rich in P and needs no further P fertiliser inputs, or P fertilisers with extremely low Cd concentrations are used.

Assuming plant breeding initiatives could deliver a chicory cultivar that could achieve annual average tissue Cd concentrations of this magnitude, there are, however, likely to be other practical challenges. For example; how many years a monoculture chicory crop can be sustained (e.g. susceptibility to pests, weeds and diseases), the ability to irrigate to remove moisture limitations to growth and also to increase Cd phytoavailability (e.g. through increased Cd diffusion) and the ability to sustain high plant tissue Cd concentrations as the most easily desorbed Cd-fractions are depleted over time.

As more than 99% of ingested Cd is excreted in dung (Van Bruwaene *et al.*, 1984; Lee *et al.*, 1994; Lee *et al.*, 1996) for a cut and carry approach to work, the harvested feed would need to be exported from the property they are grown in to remove this Cd from the farm-system completely. If the harvested feed was fed out on a feed pad within the existing farm system, the Cd excreted in animal dung would be recycled back onto paddocks receiving irrigated effluent. This scenario would likely result in increased Cd accumulation in soils receiving effluent, and no reduction in the property-mean soil Cd concentration overall.

Potentially, Cd-rich phytoaccumulator crops could be sold as stock feed to farms with low Cd soils, in doing so also reducing the receiving-properties fertiliser requirements. However, it would need to be proven that Cd-enriched chicory could be fed directly to livestock without

risk of Cd enrichment in produce destined for human consumption (e.g. milk, meat and liver / kidney tissue). However, if this was the case, then there would be little reason to reduce soil Cd concentrations in the first place, other than to reduce soil Cd concentrations for land use versatility purposes (such as for conversion under the NES (MfE, 2011)).

9.3.2.2 Manipulation of soil pH and use of soil carbon amendments

The research presented in this thesis endorses recommendations to increase soil pH to the upper end of the optimum range for the plant species, and to manage soils so as to maintain high levels of soil organic matter (FANZ, 2016). Applying organic matter / carbon amendments to the soil may also provide a means to decrease soil Cd phytoavailability (Bolan *et al.*, 2003a; Simmler *et al.*, 2013). However, care must be taken since this can also increase the rate of soil acidification (He and Singh, 1993a) reducing the overall benefit of greater Cd sorption capacity.

Practically, there are also some challenges with increasing soil organic matter/carbon, most notably the large amounts that are required to manipulate soil Cd phytoavailability. For example, the data of Simmler *et al.* (2013) and He and Singh (1993a) indicate equivalent field application rates (based on an incorporation depth of 120 mm and soil bulk density of 1.2 g cm^{-3}) of 23.2 t lignite ha^{-1} and 57.6 t sphagnum peat ha^{-1} to achieve ~30% reductions in plant tissue Cd concentration. Aside from the challenge of sourcing sufficient quantities of these carbonaceous-materials, the cost of purchasing and carting them to the farm is likely to be prohibitive to widespread adoption. For example, using lignite as an example of a relatively low-cost C-rich soil amendment, the applied and incorporated cost of lignite based on the 23.2 t ha^{-1} application rate of Simmler *et al.* (2013) ranges between \$2110 ha^{-1} to \$4314 ha^{-1} (Table 9.1), with this price heavily dependent on the distance to the lignite mine. Unless there is a direct economic incentive (e.g. a penalty from exceeding a tolerable plant tissue Cd concentration for livestock or human consumption) it is extremely unlikely that farmers will accept such costs. In particular, this is the case when there is no production benefit (or

conversely, possible yield penalties arising from increased soil N-immobilisation due to the wide C:N ratio of lignite (McLaren and Cameron, 1996; Simmler *et al.*, 2013)) as well as uncertainty as to the duration of the reduction in soil Cd phytoavailability.

Table 9.1. Estimated cost of reducing soil Cd phytoavailability using lignite as a soil amendment.

Lignite costs				
Ex-Southland mine ($ t^{-1})*	$40			
Cost of cartage to distribution depot ($ 100 km^{-1} t^{-1}) *	$10			
Total distance from lignite mine to distribution depot (km)	50	100	500	1000
Cost of cartage to distribution depot ($ t^{-1})	$5	$10	$50	$100
Cost of cartage (depot to farm) and spreading ($ t^{-1})**	$30			
Total applied cost ($ t^{-1})	$75	$80	$120	$170
Rate applied (t ha^{-1})***	23.2			
Total applied cost ($ ha^{-1})	$1,740	$1,856	$2,784	$3,944
*Incorporation costs****				
Plough or disc ($ ha^{-1})	$150			
Power harrow ($ ha^{-1})	$100			
Roller (x2) ($ ha^{-1})	$120			
Total incorporation costs ($ ha^{-1})	$370			
Total cost of amendment with lignite ($ ha^{-1})	$2,110	$2,226	$3,154	$4,314

*Denne (2013)

**Wealleans Groundspreading, personal communication, April 12, 2017

***Simmler *et al.* (2013)

****DairyNZ (2008)

Furthermore, under the scenario of land use conversion, soil total Cd concentrations need to meet maximum soil contaminant standards (SCS-Cd) that are specified under the NES. At its most stringent, a maximum soil total Cd concentration of 0.8 mg kg^{-1} is required for conversion to rural-residential land use (MfE, 2011), assessed at a sampling depth of 0-150 mm (Matthew Taylor, personal communication, 2 August 2016). As these standards are defined on soil total Cd concentration alone, addition of organic matter/carbon and manipulation of soil pH to modify soil Cd phytoavailability are of little relevance as remediation options.

9.3.2.3 Inversion-tillage

As soil Cd under permanent pasture is non-uniformly distributed in the soil profile with the greatest concentrations at the soil surface (Roberts *et al.*, 1994; Loganathan *et al.*, 1995; Loganathan and Hedley, 1997; Zanders *et al.*, 1999), soil tillage stands out as the most practical remediation option to reduce soil total Cd concentrations and decrease Cd phytoavailability.

Under arable systems, continuous soil mixing within the tillage layer is known to result in homogenisation of soil Cd concentrations within the soil tillage depth range (Roberts *et al.*, 1995; Chen *et al.*, 2009). Conventional ploughing (which turns the soil sod by approximately 45 degrees) followed by secondary cultivation techniques (e.g. discing, power harrowing etc.) will also result in soil homogenisation. This is exemplified by the differences in soil Cd, C and N concentration profiles within the Waikato and Canterbury properties of this study. Under permanent pastoral land use with little tillage history, the soil profiles of the Waikato property show a clear consistent decrease in total Cd concentration with increasing soil depth (Chapter 3, Figure 3.18). In contrast, the soil profiles of the Canterbury property show relatively uniform Cd concentrations between 0-200 mm soil depth (Chapter 3, Figure 3.25), an outcome of the regular primary and secondary tillage that has been undertaken to facilitate a rotational cropping and pasture renewal program. While this 'homogenisation-tillage' will decrease topsoil Cd concentrations, full 'inversion-tillage' (e.g. using mouldboard ploughs) will be much more effective in reducing topsoil Cd concentrations, since this technique results in the soil being flipped 180 degrees, burying Cd-enriched topsoil and bringing relatively raw, low Cd subsoil to the surface (Angers and Eriksen-Hamel, 2008; Lawrence-Smith *et al.*, 2015).

The relative impact of homogenisation-tillage versus inversion-tillage on soil profile Cd concentrations is illustrated in Figure 9.1, using site '4 Ke(A) Eff' of the Waikato property (Chapter 3, Figure 3.18). The current soil Cd depth distribution at this site is illustrated as the dashed black line (Figure 9.1) with the 0-150 mm average total Cd concentration shown as the solid black band (1.10 mg kg^{-1}). The effect of homogenisation-tillage (to 200 mm depth) on the soil Cd profile is shown by the dashed blue line, with the resultant 0-150 mm average total Cd concentration shown as the solid blue band (0.91 mg kg^{-1}). In this working, it is assumed that soil within the 0-200 mm depth range is complete homogenised through primary (e.g. ploughing) and secondary (e.g. discing) tillage. The effect of full inversion-tillage (to 200 mm depth) on the soil Cd profile is shown by the dashed red line, with the resultant 0-150 mm

average total Cd concentration shown as the solid red band (0.72 mg kg^{-1}). For this scenario, it is assumed that soil within the 0-200 mm depth range is complete inverted by deep mouldboard ploughing, with only shallow (0-50 mm) secondary cultivation. As illustrated by this example, with the burial of the most Cd-enriched topsoil beyond 150 mm depth and the deposition of low-Cd subsoil at the soil surface, inversion-tillage to a depth of 200 mm reduces 0-150 mm average total Cd concentration at this site to less than the NES rural-residential land use conversion SCS-Cd of 0.8 mg kg^{-1}, whereas homogenisation-tillage does not.

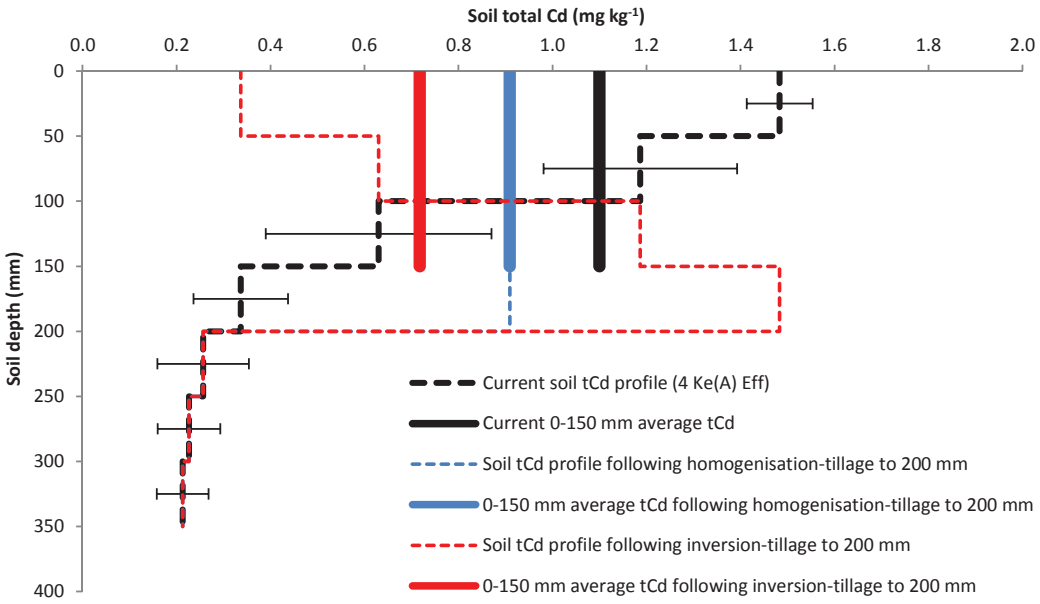

Figure 9.1. Soil profile Cd concentrations for site 4 Ke (A) Eff; Current (black dashed line) and following homogenisation-tillage (blue dashed line) or inversion-tillage (red dashed line) to 200 mm depth. Solid lines in the respective colours represent the 0-150 mm average tCd concentration for each tillage scenario.

Under a scenario where agricultural land is to be converted to rural-residential land use, the required depth of inversion-tillage will be dependent on how Cd-enriched the soil is, and also the depth distribution of this soil Cd. For this purpose, rapid in-field assessment of soil C / N profiles using NIRS technology as demonstrated in this research will be valuable to describe soil cultivation history and the likely relative depth distribution of soil Cd.

Where 0-150 mm soil Cd concentrations are greater than that demonstrated for site 4 Ke(A) Eff (Figure 9.1), greater tillage depth will likely be required. This is demonstrated in Table 9.2, where various 0-150 mm total Cd concentrations are extrapolated to soil profile Cd concentrations (to 350 mm depth, within 50 mm depth increments), assuming that the relative soil Cd concentration distribution with depth is equal to the average of the three most Cd-enriched Allophanic soils from the intact soil core study (4 Ke(A) Eff, 10 Ke(A), 22 Ke(B) Chapter 3, Figure 3.18). This analysis indicates that for the maximum 0-150 mm soil Cd concentration determined via all paddock testing (APT) in the Waikato property (1.64 mg kg^{-1}) an inversion-tillage depth of 250 mm will be required to decrease 0-150 mm total Cd to below the NES SCS of 0.8 mg kg^{-1}. For initial 0-150 mm total Cd concentrations ranging between 2.0-3.0 mg kg^{-1} (the upper end of soil Cd concentration data reported in New Zealand (Taylor *et al.*, 2007; Cavanagh, 2014a; Abraham *et al.*, 2016) an inversion-tillage depth of 300 mm would be required to produce 0-150 mm soil Cd concentrations less than 0.8 mg kg^{-1}.

Table 9.2. Determination of the required inversion-tillage depth to produce 0-150 mm total Cd concentrations less than 0.8 mg kg^{-1}, for initial 0-150 mm total Cd concentrations of; 1.64 (maximum tCd concentration determined in APT of the Waikato property) 2.0, 2.5 and 3.0 mg kg^{-1}. Where cells are shaded orange, 0.8 mg kg^{-1} has been exceeded, meaning tillage depth is insufficient. Extrapolation of 0-150 mm average total Cd concentrations to 350 mm soil depth in 50 mm depth increments was performed using soil Cd depth distribution data from intact soil core sampling sites 4 Ke(A) Eff, 10 Ke(A) and 22 Ke(B).

Soil depth range (mm)	Extrapolated soil profile tCd concentrations (mg kg^{-1}) based on a 0-150 mm average tCd concentration of:			
	1.64 (APT maximum)	2.0	2.5	3.0
0-50	2.05	2.49	3.12	3.74
50-100	1.80	2.19	2.74	3.29
100-150	1.08	1.31	1.64	1.97
150-200	0.58	0.70	0.88	1.06
200-250	0.37	0.45	0.56	0.67
250-300	0.29	0.36	0.44	0.53
300-350	0.25	0.31	0.39	0.46
Inversion-tillage depth (mm)	New 0-150 mm average tCd concentration (mg kg^{-1}) following inversion-tillage:			
200	1.15	1.40	1.75	2.11
250	0.67	0.82	1.03	1.23
300	0.41	0.50	0.63	0.75

Inversion-tillage is a feasible solution to decrease soil Cd concentrations to allow for increased land use flexibility, or to decrease Cd accumulation in Cd sensitive crops on Cd-enriched soils.

However, there is also substantial cost involved with inversion-tillage (Table 9.3), in particular, to lift soil pH and rebuild soil fertility given that subsoil brought to the soil surface is likely to be acidic and low in phosphorus and potassium (Loganathan and Hedley, 1997; Carran and Theobald, 1998). In addition, additional N-fertiliser is likely to be required for a number of years to support production, given the low organic-N concentration (Chapter 6, Figure 6.1 and Figure 6.2) and consequent low N-mineralisation capacity (Carran and Theobald, 1998) of the subsoil that is brought to the soil surface.

Costs to increase soil fertility are provided in Table 9.3, assuming an Allophanic soil with soil fertility (0-75 mm) following inversion-tillage of; pH = 5.5, plant available phosphorus (Olsen-P) = 5 mg L^{-1}, plant available potassium (QT K) = 3. To increase fertility to the target ranges defined by Roberts and Morton (2009) (pH = 5.8-6.0, Olsen-P = 20-30 mg L^{-1}, QT K = 7-10) will require approximately 5000 kg lime ha^{-1}, 220 kg P ha^{-1} and 300 kg K ha^{-1} (based on the typical amounts of lime, P and K required to shift pH, Olsen-P and QT K as defined by Roberts and Morton (2009)). Further to this, it is assumed that on average, an extra 100 kg N ha^{-1} y^{-1} will be required over 5 years following deep inversion tillage.

Table 9.3. Cost of remediation via inversion-tillage.

*Tillage costs**						*$ ha^{-1}*
Deep inversion plough						$200
Power harrow						$100
Roller (x2)						$120
Total tillage costs						$420
Capital lime and fertiliser costs	*Soil fertility:*			*Lime, P, K or N required (kg ha^{-1})***	*Applied cost ($ kg^{-1})****	*$ ha^{-1}*
	Post inversion-tillage	*Target range***	*Increase required*			
Soil pH	5.5	5.8-6.0	0.5	5000	$0.05	$250
Plant available phosphorus (Olsen-P)	5	20-30	20	220	$3.00	$660
Plant available potassium (QT K)	3	7-10	5	300	$1.25	$375
Additional N-fertiliser applied over 5 years post inversion-tillage	-	-	-	500	$1.30	$650
Total additional fertiliser cost						$1,935
Total cost to remediate via inversion tillage						$2,355

*DairyNZ (2008)
**Roberts and Morton (2009)
***Approximate fertiliser and lime costs as at Feb 2017 (www.ballance.co.nz and www.ravensdown.co.nz).

Total cost of inversion tillage (Table 9.3) is therefore comparable to the cost of incorporating lignite (Table 9.1). However, the advantage with inversion tillage is that topsoil Cd concentrations will be substantially reduced (Figure 9.1), as opposed to the incorporation of C-rich material, which only reduces the phytoavailability of existing soil total Cd concentrations. This is an important aspect with regard to land use flexibility under the NES (MfE, 2011). The impact of inversion tillage on plant Cd uptake and accumulation does, however, need to be quantified in field research trials.

A final, but important, consideration with inversion tillage is that low-Cd P fertilisers are used to rebuild soil P fertility, so as to minimise 'repeat' soil Cd accumulation in the soil re-development phase. For this purpose, phosphoric acid-based P fertilisers (such as di-ammonium phosphate or triple superphosphate) are likely to be the preferred option, since they typically contain lower Cd concentrations than sulphuric acid-based P fertilisers such as superphosphate (FANZ, 2016) and are far cheaper and more common than nitric acid-based P fertilisers.

9.4 Future research requirements

Following the knowledge improvements that have been made in the course of this research, there are several knowledge gaps that justify further research, summarised as below:

1) Animal grazing trials (both sheep and dairy cattle) are recommended to evaluate whether the original animal Cd accumulation models are reliable and relevant for Cd-enriched plant forage species such as chicory and plantain, given their tissue Cd concentrations far exceed that of the calibrate datasets of the original model (Lee *et al.*, 1994; Lee *et al.*, 1996) and since concurrent accumulation of other divalent metals such as zinc, copper and cobalt (Barry *et al.*, 2001; Harrington *et al.*, 2006; Hoskin *et al.*, 2006) may be antagonistic to metallothionein-sorption of Cd in the liver/kidney tissues of grazing livestock (Parker *et al.*, 2008). Importantly, if Cd accumulation in the liver/kidney of grazing livestock is found to

be lower than that predicted based on intake, then these trials need to identify where this excess Cd is being expressed.

2) Plant breeding initiatives should be explored to investigate opportunities to decrease vegetative tissue Cd concentrations in Cd accumulating crops such as chicory and plantain. This seems a pragmatic approach to reducing animal (and human) exposure to Cd, given that high tissue Cd concentrations can occur in these plant species even at relatively low soil total Cd concentrations. Dependent on the outcome of the animal feeding trial (1) there is also potential to look at plant breeding initiatives to produce chicory cultivars with increased capacity for Cd accumulation in vegetative tissue, for the purpose of phytoremediation.
3) Recent research has identified that Cd isotope ratios specific to different P fertilisers can be used to trace the origins of accumulated soil Cd (Hartland, 2016; Salmanzadeh *et al.*, 2016b). An opportunity for future research is to extend this Cd isotope analysis technique to plant tissue, to understand the relative contribution of 'recent' versus 'historic' anthropogenic soil Cd inputs to plant Cd accumulation in chicory.
4) Field research should be conducted to quantify / validate the reduction in topsoil total Cd concentration that is achieved with inversion tillage, and to quantify the reduction in plant Cd uptake and accumulation that is achieved, relative to that from the incorporation of C-rich soil amendments / modification of pH. In particular, this would be of interest for deep rooting, 'Cd-accumulator' plant species such as chicory.
5) Ongoing research is needed to develop Cd-free (or at least, extremely low Cd) P fertilisers for use in situations where soil Cd concentrations have already been enriched (e.g. Tier 2-3 of the TFMS) by historic P fertiliser application, and in particular, where Cd-sensitive plant species such as chicory and plantain are intended to be grown. While current decadmiation technologies (e.g. calcination) are not economically viable (Oosterhuis *et al.*, 2000), increased global dependence on the Cd-rich Moroccan P rock deposits (de Ridder *et*

al., 2012) will mean that there will be need for technologies to reduce Cd concentration in P fertilisers, and also to improve P use efficiency. Furthermore, there is current regulatory development to substantially decrease Cd concentration in P fertilisers used in the EU (EC, 2016) as well as increase the recycling and reuse of P from organic waste streams (de Ridder *et al.*, 2012). Such regulatory development has the potential to directly influence P fertiliser management in New Zealand (e.g. in the form of a non-tariff trade barrier).

9.5 What does this research mean for New Zealand farmers?

This research provides the first documented assessment of soil Cd variability within long-term dairy farms. Importantly, the linkage of soil Cd variability in these properties to anthropogenic (e.g. P fertiliser and soil tillage history) and lithogenic (e.g. soil mineralogy and organic matter content) drivers provides a means of extrapolating and understanding the variability expected in other properties. Under the Tiered Fertiliser Management System, for long-term dairy farms with Cd-enriched soils (e.g. Tier 2-4) this will be important to ensure that soil Cd assessment is robust and comprehensive. NIRS technology shows potential for rapid, low cost assessment of soil tillage history and the associated distribution of Cd in the soil profile. This will help to inform farmers of site-specific tillage depth requirements, for the purpose of reducing soil total Cd to a target/threshold (e.g. regulatory) concentration, or for decreasing soil Cd phytoavailability. Options for farmers to decrease soil Cd solubility in Cd-enriched soils are desirable, especially given that research within this PhD project has identified that chicory and plantain are sensitive to soil Cd phytoavailability, accumulating significantly greater vegetative-tissue Cd concentrations than traditional ryegrass and white clover based pastures. Due to the favourable characteristics of chicory and plantain (e.g. drought resilience and multi-year persistence, high yield and high feed quality, increased micronutrient supply and reduced livestock exposure to internal parasites and facial eczema) the popularity and prevalence of these species in New Zealand livestock grazing systems is likely to increase into the future.

With these plant species identified as Cd-accumulators, farmers are now able to better manage livestock dietary Cd exposure. Given the knowledge of factors influencing spatial variability of soil Cd and soil factors influencing its solubility (e.g. soil total Cd, pH, organic matter) livestock dietary Cd exposure can be managed through selective planting of these species into areas of the farm with lower soil Cd phytoavailability. Furthermore, although soil pH has traditionally been maintained within an agronomic optimum range of 5.8-6.0, increasing soil pH to a minimum of 6.5 is a practical management strategy available to farmers for decreasing livestock dietary Cd exposure when grazing chicory forage stands.

REFERENCES

Abe, T., Fukami, M., Ogasawara, M., 2008. Cadmium accumulation in the shoots and roots of 93 weed species. Soil Science & Plant Nutrition 54, 566-573.

Abraham, E., Cavanagh, J., Wood, P., Pearson, A., Mladenov, P., 2016. Cadmium in New Zealand's agriculture and food systems. In: Currie, L.D., Singh, R. (Eds.), Integrated nutrient and water management for sustainable farming. Occasional Report No. 29. http://flrc.massey.ac.nz/publication.html. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, p. 13.

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

Anderson, K.A., 1996. Micro-digestion and ICP-AES analysis for the determination of macro and micro elements in plant tissues. Atomic Spectroscopy 17, 30-33.

Andersson, A., Hahlin, M., 1981. Cadmium effects from phosphorus fertilization in field experiments. Swedish Journal of Agricultural Research 11, 3-10.

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.

Angers, D.A., Eriksen-Hamel, N.S., 2008. Full-inversion tillage and organic carbon distribution in soil profiles: A meta-analysis. Soil Science Society of America journal 72, 1370-1374.

Atta, S.K., Mohammed, S.A., Van Cleemput, O., Zayed, A., 1996. Transformations of iron and manganese under controlled E(h), E(h)-pH conditions and addition of organic matter. Soil Technology 9, 223-237.

Backes, C.A., McLaren, R.G., Rate, A.W., Swift, R.S., 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Science Society of America 59, 778-785.

Barry, T.N., Molan, A.L., Wilson, P.R., Lopez-Villalobos, N., Schreurs, N.M., Duncan, A.J., 2001. Chicory as an alternative forage for deer health. In: Wilson, P.R. (Ed.), Proceedings of a Deer Course for Veterinarians No. 18. Deer Branch of the New Zealand Veterinary Association, pp. 122-127.

Bešter, P.K., Lobnik, F., Eržen, I., Kastelec, D., Zupan, M., 2013. Prediction of cadmium concentration in selected home-produced vegetables. Ecotoxicology and Environmental Safety 96, 182-190.

Bhatti, S.M., Anderson, C.W.N., Stewart, R.B., Robinson, B.H., 2013. Risk assessment of vegetables irrigated with arsenic-contaminated water. Environmental Science. Processes & Impacts 15, 1866-1875.

Bingham, F.T., Page, A.L., Mahler, R.J., Ganje, T.J., 1975. Growth and cadmium accumulation of plants grown on a soil treated with a cadmium-enriched sewage sludge. Journal of Environmental Quality 4, 207-211.

Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. Methods for Chemical Analysis of Soils. Scientific Report 80. New Zealand Soil Bureau. 103 p.

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., Duraisamy, P., Mani, A., 2003a. Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid compost addition. Plant and Soil 256, 231-241.

Bolan, N.S., Adriano, D.C., Duraisamy, P., Mani, A., Arulmozhiselvan, K., 2003b. Immobilization and phytoavailability of cadmium in variable charge soils. I. Effect of phosphate addition. Plant & Soil 250, 83-94.

Bolan, N.S., Adriano, D.C., Mani, P.A., Duraisamy, A., 2003c. 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., Khan, M.A.R., Tillman, R.W., Syers, J.K., 1999a. The effects of anion sorption on sorption and leaching of cadmium. Australian Journal of Soil Research 37, 445-460.

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

Bollag, J.M., Barabasz, W., 1979. Effect of heavy metals on the denitrification process in soil. Journal of Environmental Quality 8, 196-201.

Bramley, R.G.V., 1990. Cadmium in New Zealand agriculture. New Zealand Journal of Agricultural Research 33, 505-519.

Carran, R.A., Theobald, P.W., 1998. Long-term effects of grazing on the fertility of soils. Proceedings of the New Zealand Grassland Association 60, Nelson, New Zealand, pp. 75-78.

Carrick, S., Cavanagh, J., Scott, J., McLeod, M., 2014. Understanding phosphorus, nitrogen and cadmium transfer through a young stony soil. In: L.D., C., Christensen, C.L. (Eds.), Nutrient management for the farm, catchment and community. http://flrc.massey.ac.nz/publications.html. Occasional Report No. 27. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, p. 11.

Cavanagh, J., 2012. Working towards New Zealand risk-based soil guideline values for the management of cadmium accumulation on productive land. Ministry for Primary Industries Technical Paper No: 2012/06. Wellington, New Zealand. 71 p. http://www.mpi.govt.nz/news-resources/publications.aspx.

Cavanagh, J., 2014a. Review of models to predict cadmium accumulation in agricultural soils. Report prepared for Fertiliser Association of New Zealand and Ministry for Primary Industries. LC 1820. Landcare Research. Lincoln, New Zealand. 20 p.

Cavanagh, J., 2014b. Status of cadmium in New Zealand soils: 2014. Report prepared for Fertiliser Association of New Zealand and Ministry for Primary Industries. Landcare Research. Lincoln, New Zealand. 44 p. http://www.fertiliser.org.nz/Site/research/completed_research/default.aspx.

Chaney, R.L., Angle, J.S., McIntosh, M.S., Reeves, R.D., Li, Y.M., Brewer, E.P., 2005. Using hyperaccumulator plants to phytoextract soil Ni and Cd. Zeitschrift für Naturforschung C 60, 190-198.

Chaney, R.L., Ryan, J.A., Li, Y., Brown, S.L., 1999. Soil cadmium as a threat to human health. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers Dordrecht, The Netherlands, pp. 219-256.

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

Charlatchka, R., Cambier, P., 2000. Influence of reducing conditions on solubility of trace metals in contaminated soils. Water, Air, and Soil Pollution 118, 143-167.

Chatterjee, S., Mitra, A., S., D., Veer, V., 2013. Phytoremediation protocols: an overview. In: Gupta, D.K. (Ed.), Plant-based remediation processes. Soil Biology, Volume 35. Springer, Berlin, pp. 1-18.

Chen, W., Laosheng, W., Chang, A.C., Hou, Z., 2009. Assessing the effect of long term crop cultivation on distribution of Cd in the root zone. Ecological Modelling 220, 1836-1843

Chien, S.H., Carmona, G., Prochnow, L.I., Austin, E.R., 2003. Cadmium availability from granulated and bulk-blended phosphate-potassium fertilizers. Journal of Environmental Quality 32, 1911-1914.

Cho, Y.A., Kim, J., Woo, H.D., Kang, M., 2013. Dietary cadmium intake and the risk of cancer: a meta-analysis. PLoS ONE 8(9): e75087. doi:10.1371/journal.pone.0075087. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3775812/.

Christensen, T.H., 1984. Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. Water, Air, and Soil Pollution 21, 105-114.

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.

Coppola, S., Dumontet, S., Pontonio, M., Basile, G., Marino, P., 1988. Effect of cadmium-bearing sewage sludge on crop plants and microorganisms in two different soils. Agriculture, Ecosystems and Environment 20, 181-194.

Cornu, J.Y., Denaix, L., Schneider, A., Pellerin, S., 2007. Temporal evolution of redox processes and free Cd dynamics in a metal-contaminated soil after rewetting. Chemosphere 70, 306-314.

Cornu, S., Cattle, J.A., Samouelian, A., Laveuf, C., Guilherme, L.R.G., Alberic, P., 2009. Impact of redox cycles on manganese, iron, cobalt, and lead in nodules. Soil Science Society of America journal 73, 1231-1241.

Crush, J.R., Evans, J.P.M., 1990. Shoot growth and herbage element concentrations of 'Grasslands Puna' chicory (*Cichorium intybus L.*) under varying soil pH. Proceedings of the New Zealand Grassland Association 51, Ashburton, New Zealand, pp. 163-166.

DairyNZ, 2008. Growing a high yielding crop. DairyNZ Farmfact 1-62. 4 p. https://www.dairynz.co.nz/media/253747/1-62_Turnips_Growing_a_high_yielding_crop.pdf.

Dar, G.H., Mishra, M.M., 1994. Influence of cadmium on carbon and nitrogen mineralization in sewage sludge amended soils. Environmental Pollution 84, 285-290.

de Livera, J., McLaughlin, M.J., Hettiarachchi, G.M., Kirby, J.K., Beak, D.G., 2011. Cadmium solubility in paddy soils: Effects of soil oxidation, metal sulfides and competitive ions. Science of the Total Environment 409, 1489-1497.

De Pieri, L.A., Buckley, W.T., Kowalenko, C.G., 1997. Cadmium and lead concentrations of commercially grown vegetables and of soils in the Lower Fraser Valley of British Columbia. Canadian Journal of Soil Science 77, 51-57.

de Ridder, M., de Jong, S., Polchar, J., Lingemann, S., 2012. Risks and opportunities in the global phosphate rock market. Robust strategies in times of uncertainty. Report No. 17 | 12 | 12. The Hague Centre for Strategic Studies. The Hague, The Netherlands. 102 p.

de Vries, W., Romkens, P.F.A.M., Schutze, G., 2007. Critical soil concentrations of cadmium, lead and mercury in view of health effects on humans and animals. Reviews of Environmental Contamination and Toxicology 191, 91-130.

DeLaune, R.D., Reddy, K.R., 2005. Redox Potential. In: Hillel, D. (Ed.), Encyclopedia of Soils in the Environment. Academic Press, Amsterdam, The Netherlands, pp. 366-371.

Denne, T., 2013. Coal prices in the New Zealand markets: 2013 update. Report for MBIE. COVEC. Auckland, New Zealand. 19 p. http://www.mbie.govt.nz/info-services/sectors-industries/energy/energy-data-modelling/technical-papers/coal-prices-in-new-zealand-markets.

Doelman, P., Haanstra, L., 1986. Short and long term effects of heavy metals on urease activity in soils. Biology and Fertility of Soils 2, 213-218.

Dunbar, K.R., McLaughlin, M.J., Reid, R.J., 2003. The uptake and partitioning of cadmium in two cultivars of potato (*Solanum tuberosum* L.). Journal of Experimental Botany 54, 349-354.

Dusek, L., 1995. The effect of cadmium on the activity of nitrifying populations in two different grassland soils. Plant and Soil 177, 43-53.

EC, 2013. Commission Regulation (EU) No. 1275/2013 of 6 December 2013 amending Annex I to Directive 2002/32/EC of the European Parliament and of the Council as regards

maximum levels for arsenic, cadmium, lead, nitrites, volatile mustard oil and harmful botanical impurities. 7 p. http://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32013R1275&qid=1474193581503.

EC, 2014. Commission Regulation (EU) No. 488/2014 of 12 May 2014 amending Regulation (EC) No. 1881/2006 as regards maximum levels of cadmium in foodstuffs. 5 p. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32014R0488&from=EN.

EC, 2016. Factsheet on cadmium in fertilisers. Subject: Proposed cadmium limits for CE marked phosphate fertiliser in the new Fertilising Products Regulation - justification, impact and compatibility with international trade rules. 17 October 2016. European Commission. Brussels. 10 p. https://circabc.europa.eu/webdav/CircaBC/GROW/fertipub/Library/2.%20General%20information/Factsheet%20on%20Cd%20in%20P-fertilisers.pdf.

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.

Florijn, P.J., Van Beusichem, M.L., 1993. Uptake and distribution of cadmium in maize inbred lines. Plant and Soil 150, 25-32.

Flower, K.C., Crabtree, W.L., 2011. Soil pH change after surface application of lime related to the levels of soil disturbance caused by no-tillage seeding machinery. Field Crops Research 121, 75-87.

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.

Fraser, T.J., Rowarth, J.S., 1996. Legumes, herbs or grass for lamb performance?. Proceedings of the New Zealand Grassland Association 58, Oamaru, New Zealand, pp. 49-52.

FSANZ, 2011. Standard 1.4.1. Contaminants and natural toxicants. Food Standards Australia New Zealand. 8 p. https://www.comlaw.gov.au/Details/F2015C00052.

Gillingham, A.G.G., 1980. Phosphorus uptake and return in grazed, steep hill pastures. New Zealand Journal of Agricultural Research 23, 313-321.

Goodall, V.C., 1951. The day and night grazing system. Proceedings of the New Zealand Grassland Association 13, New Plymouth, New Zealand, pp. 86-94.

Gotoh, S., Patrick, W.H., 1972. Transformations of manganese in a waterlogged soil as affected by redox potential and pH. Soil Science Society of America Proceedings 36, 738-742.

Gotoh, S., Patrick, W.H., 1974. Transformations of iron in a waterlogged soil as influenced by redox potential and pH. Soil Science Society of America Proceedings 38, 66-71.

Grafton, M.C.E., Yule, I.J., Manning, M.J., 2013. A review of the economic impact of high levels of variance in fertiliser spreading systems. Proceedings of the New Zealand Grassland Association 75, Tauranga, New Zealand, pp. 131-136.

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.

Grant, C.A., Clarke, J.M., Duguid, S., Chaney, R.L., 2008. Selection and breeding of plant cultivars to minimize cadmium accumulation. Science of the Total Environment 390, 301-310.

Gray, C.W., McDowell, R.W., 2016. Cadmium losses from a New Zealand organic soil. New Zealand Journal of Agricultural Research 59, 185-193.

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., 2001. Cadmium concentrations in some New Zealand wheat grain. New Zealand Journal of Crop and Horticultural Science 29, 125-136.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., 2003a. Atmospheric accessions of heavy metals to some New Zealand pastoral soils. The Science Of The Total Environment 305, 105-115.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., 2003b. Cadmium leaching from some New Zealand pasture soils. European Journal of Soil Science 54, 159-166.

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. The effect of long-term phosphatic fertiliser applications on the amounts and forms of cadmium in soils under pasture in New Zealand. Nutrient Cycling in Agroecosystems 54, 267–277.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 1999c. 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., 1999d. 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.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., Condron, L.M., 2000. Fractionation of soil cadmium from some New Zealand soils. Communications in Soil Science and Plant Analysis 31, 1261-1273.

Gupta, D.K., 2013. Preface. In: Gupta, D.K. (Ed.), Plant-based remediation processes. Soil Biology, Volume 35. Springer, Berlin, pp. vii-ix.

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.

Harrington, K.C., Thatcher, A., Kemp, P.D., 2006. Mineral composition and nutritive value of some common pasture weeds. New Zealand Plant Protection Society, pp. 261-265.

Hartland, A., 2016. An isotopic evaluation of the apparent plateau in New Zealand soil cadmium accumulation: mixing model evaluation. Report to the Fertiliser Association of New Zealand. University of Waikato. Hamilton, New Zealand. 15 p.

Havlin, J.L., Beaton, J.D., Tisdale, S.L., Nelson, W.L., 2005. Soil fertility and fertilisers. An introduction to nutrient management (7th Edition). Peason Prentice Hall, New Jersey, United States of America. 515 p.

He, Q.B., Singh, B.R., 1993a. Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. Journal of Soil Science 44, 641-650.

He, Q.B., Singh, B.R., 1993b. 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.

He, Q.B., Singh, B.R., 1994. Cadmium uptake by crops from phosphorus fertilisers: I. Yield and cadmium concentration. Water, Air and Soil Pollution 74, 251-265.

Healy, W.B., 1967. Ingestion of soil by sheep. Proceedings of the New Zealand Society of Animal Production 27, pp. 109-120.

Healy, W.B., 1968. Ingestion of soil by dairy cows. New Zealand Journal of Agricultural Research 11, 487-499.

Helmke, P.A., 1999. Chemistry of cadmium in soil solution. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 39-64.

Hernandez-Soriano, M.C., Jimenez-Lopez, J.C., 2012. Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals. The Science Of The Total Environment 423, 55-61.

Hindersmann, I., Mansfeldt, T., 2014. Trace element solubility in a multimetal-contaminated soil as affected by redox conditions. Water, Air, and Soil Pollution 225, 1-20 (Article 2158).

Hinsinger, P., Plassard, C., Tang, C., Jaillard, B., 2003. Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: A review. Plant and Soil 248, 43-59.

Horrell, R., Metherell, A.K., Ford, S., Doscher, C., 1999. Fertiliser evenness - losses and costs: A study on the economic benefits of uniform applications of fertiliser. Proceedings of the New Zealand Grassland Association 61, Hawkes Bay, New Zealand, pp. 215–220.

Hoskin, S.O., Wilson, P.R., Ondris, M., Bunod, A.H., 2006. The feeding value of forage herbs: studies with red deer. Proceedings of the New Zealand Grasslands Association 68, Dunedin, New Zealand, pp. 199-204.

IARC, 1993. Beryllium, cadmium, mercury and exposure in the glass manufacturing industry. World Health Organisation International Agency for Research on Cancer. http://monographs.iarc.fr/ENG/Monographs/vol58/.

IBM Corp, 2013. IBM SPSS Statistics for Windows, Version 22.0. Released 2013. IBM Corp, Armonk, NY.

Iu, K.L., Pulford, I.D., Duncan, H.J., 1981. Influence of waterlogging and lime or organic matter additions on the distribution of trace metals in an acid soil - I. Manganese and iron. Plant and Soil 59, 317-326.

Jarup, L., Akesson, A., 2009. Current status of cadmium as an environmental health problem. Toxicology and Applied Pharmacology 238, 201-208.

Jeyakumar, P., Loganathan, P., Anderson, C.N., Sivakumaran, S., McLaren, R., 2014. Comparative tolerance of *Pinus radiata* and microbial activity to copper and zinc in a soil treated with metal-amended biosolids. Environmental Science and Pollution Research 21, 3254-3263.

John, M.K., Chuah, H.H., VanLaerhoven, C.J., 1972. Cadmium contamination of soil and its uptake by oats. Environmental science & technology 6, 555-557.

Kahle, P., Möller, J., Baum, C., Gurgel, A., 2013. Tillage-induced changes in the distribution of soil organic matter and the soil aggregate stability under a former short rotation coppice. Soil & Tillage Research 133, 49-53.

Kashem, M.A., Singh, B.R., 2001. Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. Nutrient Cycling in Agroecosystems 61, 247-255.

Kelliher, F.M., Condron, L.M., Cook, F.J., Black, A., 2012. Sixty years of seasonal irrigation affects carbon storage in soils beneath pasture grazed by sheep. Agriculture, ecosystems & environment 148, 29-36.

Kim, K., Owens, G., Naidu, R., 2009. Heavy metal distribution, bioaccessibility, and phytoavailability in long-term contaminated soils from Lake Macquarie, Australia. Australian Journal of Soil Research 47, 166-176.

Kim, N., 2005. Cadmium accumulation in Waikato soils. Technical Report 2005/51. August 2005. Environment Waikato. Hamilton, New Zealand. 143 p. http://www.waikatoregion.govt.nz/Services/Publications/Technical-Reports/TR-200551/.

Kim, N.D., Fergusson, J.E., 1992. Adsorption of cadmium by an aquent New Zealand soil and its components. Australian Journal of Soil Research 30, 159-167.

Kovács, B., Prokisch, J.G., Z , Kovács, A.B., Palencsár, A.J., 2000. Analytical methods and quality assurance. Communications in Soil Science and Plant Analysis 31, 1949-1963.

Kusumo, B.H., 2009. Development of field techniques to predict soil carbon, soil nitrogen and root density from soil spectral reflectance (Unpublished doctoral thesis). Massey University, Palmerston North, New Zealand.

Kusumo, B.H., Hedley, C.B., Hedley, M.J., Hueni, A., Tuohy, M.P., Arnold, G.C., 2008. The use of diffuse reflectance spectroscopy for in situ carbon and nitrogen analysis of pastoral soils. Australian Journal of Soil Research 46, 623–635.

Kusumo, B.H., Hedley, M.J., Hedley, C.B., Tuohy, M.P., 2011. Measuring carbon dynamics in field soils using soil spectral reflectance: prediction of maize root density, soil organic carbon and nitrogen content. Plant and Soil 338, 233–245.

Landcare Research, 2015. Soil Orders from the New Zealand Soil Classification (NZSC). Landcare Research. http://soils.landcareresearch.co.nz/contents/SoilNames_NZSoilClassification_SoilOrders.aspx?currentPage=SoilNames_NZSoilClassification_SoilOrders%26.

Lawrence-Smith, E., Curtin, D., Beare, M., Kelliher, F., 2015. Potential applications of full inversion tillage to increase soil carbon storage during pasture renewal in New Zealand. A Plant & Food Research report prepared for: NZAGRC. Milestone No. 61925. Contract No. 31874. Job code: P/442029/08. PFR SPTS No. 12101. 54 p.

Ledgard, S., Brier, G., 2004. Estimation of the proportion of animal excreta transferred to the farm dairy effluent system. Report prepared for the Ministry of Agriculture and Forestry. AgResearch. Hamilton, New Zealand.

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.

Levi-Minzi, R., Petruzzelli, G., 1984. Influence of phosphate fertilizers on Cd solubility in soil. Water, Air and Soil Pollution 23, 423-429.

Li, F., Okazaki, M., Zhou, Q., 2003. Evaluation of Cd uptake by plants estimated from total soil Cd, pH, and organic matter. Bulletin of Environmental Contamination and Toxicology 71, 714-721.

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.

Li, Y.M., Chaney, R.L., Schneiter, A.A., Miller, J.F., Elias, E.M., Hammond, J.J., 1997. Screening for low grain cadmium phenotypes in sunflower, durum wheat and flax. Euphytica 94, 23-30.

Li, Z., McLaren, R.G., Metherell, A.K., 2001. Cobalt and manganese relationships in New Zealand soils. New Zealand Journal of Agricultural Research 44, 191-200.

Liu, J., Qian, M., Cai, G., Yang, J., Zhu, Q., 2007. Uptake and translocation of Cd in different rice cultivars and the relation with Cd accumulation in rice grain. Journal of Hazardous Materials 143, 443-447.

Liu, M., Yanai, J., Jiang, R., Zhang, F., McGrath, S., Zhao, F., 2008. Does cadmium play a physiological role in the hyperaccumulator *Thlaspi caerulescens*? Chemosphere 71, 1276-1283.

Loganathan, P., Hedley, M.J., 1997. Downward movement of cadmium and phosphorus from phosphatic fertilisers in a pasture soil in New Zealand. Environmental Pollution 95, 319-324.

Loganathan, P., Hedley, M.J., Grace, N.D., Lee, J., Cronin, S.J., Bolan, N.S., Zanders, J.M., 2003. Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review. Australian Journal of Soil Research 41, 501-532.

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.

Lovley, D.R., 1995. Microbial reduction of iron, manganese, and other metals. Advances in Agronomy 54, 175-231.

MAF, 2008. Cadmium in New Zealand Agriculture. Report for the Cadmium Working Group. Ministry of Agriculture and Forestry. Wellington, New Zealand. 85 p. http://www.mpi.govt.nz/news-resources/publications.aspx?title=Cadmium.

MAF, 2011. Cadmium and New Zealand agriculture and horticulture: a strategy for long term risk management. Technical Paper No: 2011/03. Ministry of Agriculture and Forestry. Wellington, New Zealand. 27 p. http://www.mpi.govt.nz/news-resources/publications.aspx?title=Cadmium.

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.

Malley, D.F., Martin, P.D., Ben-Dor, E., 2004. Application in analysis of soils. In: Barbarick, K.A., Roberts, C.A., W.A., D., Workman, J.J., Reeves III, J.B., Al-Amoodi, L. (Eds.), Near-infrared spectroscopy in agriculture. Agronomy Monograph No. 44. American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc., Madison, WI, pp. 729-784.

Mann, S.S., Ritchie, G.S., 1995. Forms of cadmium in sandy soils after amendment with soils of higher fixing capacity. Environmental Pollution 87, 23-29.

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.

Martin, H.W., Young, T.R., Kaplan, D.I., Simon, L., Adriano, D.C., 1996. Evaluation of three herbaceous index plant species for bioavailability of soil cadmium, chromium, nickel and vanadium. Plant and Soil 182, 199-207.

Martin, T.D., Creed, J.T., Brockhoff, C.A., 1994. Sample preparation procedure for spectrochemical determination of total recoverable elements. U.S. Environmental Protection Agency Report, Revision 2.8, EMMC Version. 12 p.

Masscheleyn, P.H., Delaune, R.D., Patrick, W.H., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science and Technology 25, 1414-1419.

Maxwell, T.M.R., Moir, J.L., Edwards, G.R., 2013. Phosphorus response and efficiency of four adventive annual clovers grown in a New Zealand high country soil under glasshouse conditions. New Zealand Journal of Agricultural Research 56, 203-214.

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.

McBride, M.B., 1989. Reactions controlling heavy metal solubility in soils. Advances in Soil Sciences 10, 1-56.

McBride, M.B., 2002. Cadmium uptake by crops estimated from soil total Cd and pH. Soil Science 167, 62-67.

McDowell, R.W., 2012. The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. New Zealand Journal of Agricultural Research 55, 133-146.

McDowell, R.W., Cosgrove, G.P., 2015. Selection of a legume to use in a low phosphorus loss pasture. New Zealand Journal of Agricultural Research (Submitted).

McDowell, R.W., Taylor, M.D., Stevenson, B.A., 2013. Natural background and anthropogenic contributions of cadmium to New Zealand soils. Agriculture, Ecosystems and Environment 165, 80-87.

McGrath, S.P., 1999. Adverse effects of cadmium on soil microflora and fauna. In: McLaughlin, M.J., Singh, B.R. (Eds.), Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 199-218.

McLaren, R.G., Cameron, K.C., 1996. Soil science : sustainable production and environmental protection (2nd Edition). Oxford University Press; Auckland, New Zealand. 304 p.

McLaughlin, M.J., Maier, N.A., Freeman, K., Tiller, K.G., Williams, C.M.J., Smart, M.K., 1995. Effect of potassic and phosphatic fertilizer type, fertilizer Cd concentration and zinc rate on cadmium uptake by potatoes. Nutrient Cycling in Agroecosystems 40, 63-70.

McLaughlin, M.J., Maier, N.A., Rayment, G.E., Sparrow, L.A., Berg, G., McKay, A., Milham, P., Merry, R.H., Smart, M.K., 1997. Cadmium in Australian potato tubers and soils. Journal of Environmental Quality 16.

McLaughlin, M.J., Palmer, L.T., Tiller, K.G., Beech, T.A., Smart, M.K., 1994a. Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers. Journal of Environmental Quality 23, 1013-1018.

McLaughlin, M.J., Tiller, K.G., Naidu, R., Stevens, D.P., 1996. Review: The behaviour and environmental impact of contaminants in fertilisers. Australian Journal of Soil Research 34, 1-54.

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., 1994b. Effect of cultivar on uptake of cadmium by potato tubers. Australian Journal of Agricultural Research 45, 1483-1495.

MfE, 2011. Methodology for deriving standards for contaminants in soil to protect human health. Ministry for the Environment. Wellington, New Zealand. 207 p. http://www.mfe.govt.nz/publications/hazardous/deriving-standards-for-contaminants-in-soil/index.html.

MIA, 2015. Meat Industry Association 2015 Annual Report. Wellington, New Zealand. 66 p. http://www.mia.co.nz/docs/annual_reports/MIA_Annual_Report_2015.pdf.

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.

Morrison, I., 1988. Monitoring of pesticides and heavy metals in dairy products. Proceedings of the Nutrition Society of New Zealand, 13, pp. 74-79.

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., Sinclair, A.G., Morrison, J.D., Smith, L.C., Dodds, K.G., 1998a. Balanced and adequate nutrition of phosphorus and sulphur in pasture. New Zealand Journal of Agricultural Research 41, 487-496.

Morton, J.D., Wheeler, D.M., Smith, N.S., 1998b. 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.

Moulis, J.-M., Thevenod, F., 2010. New perspectives in cadmium toxicity: an introduction. BioMetals 23, 763-768.

MPI, 2012. Dairy National Chemical Contaminants Programme - Raw Milk Result Summary 2011/12. . Ministry for Primary Industries. Wellington, New Zealand. 44 p. http://www.foodsafety.govt.nz/elibrary/industry/dairy-nccp-results-summary.pdf.

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

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.

Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D., Tiller, K.G., 1997. Cadmium sorption and transport in variable charge soils: a review. Journal of Environmental Quality 26, 602-617.

Narteh, L.T., Sahrawat, K.L., 1999. Influence of flooding on electrochemical and chemical properties of West African soils. Geoderma 87, 179-207.

Nawrot, T.S., Staessen, J.A., Roels, H.A., Munters, E., Cuypers, A., Richart, T., Ruttens, A., Smeets, K., Clijsters, H., Vangronsveld, J., 2010. Cadmium exposure in the population: from health risks to strategies of prevention. BioMetals 23, 769-782.

Nordberg, G.F., 2009. Historical perspectives on cadmium toxicology. Toxicology and Applied Pharmacology 238, 192-200.

Norrish, K., 1981. Review paper on mineralogy. In: Rankin, P.C., Churchman, G.J. (Eds.), Soils with variable charge conference proceedings. Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt, New Zealand, pp. 17-29.

NZWWA, 2003. Guidelines for the safe application of biosolids to land in New Zealand. New Zealand Water and Wastes Association. Wellington, New Zealand. 183 p. http://www.nzwwa.org.nz/Category?Action=View&Category_id=106.

O'Connor, M.B., Longhurst, R.D., Johnston, T.J.M., Portegys, F.N., 2001. Fertiliser requirements for peat soils in the Waikato region. Proceedings of the New Zealand Grasslands Association 63, Hamilton, New Zealand, pp. 47-51.

Oborn, I., Jansson, G., Johnsson, L., 1995. A field study on the influence of soil pH on trace element levels in spring wheat (*Triticum aestivum*), potatoes (*Solanum tuberosum*) and carrots (*Daucus carota*). Water, Air and Soil Pollution 85, 835-840.

Oliver, D.P., Hannam, R., Tiller, K.G., Wilhelm, N.S., Merry, R.H., Cozens, G.D., 1994. The effects of zinc fertilisation on cadmium concentration in wheat grain. Journal of Environmental Quality 23, 705-711.

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.

Oosterhuis, F.H., Brouwer, F.M., Wijnants, H.J., 2000. A possible EU wide charge on cadmium in phosphate fertilisers: economic and environmental implications. Final report to the European Commission E-00/02. Institute for Environmental Studies, Vrije Universiteit. Amsterdam, The Netherlands. 85 p. https://research.vu.nl/en/publications/a-possible-eu-wide-charge-on-cadmium-in-phosphate-fertilisers-eco.

Page, A.L., Bingham, F.T., 1973. Cadmium residues in the environment. Residue Reviews 48, 1-44.

Page, V., Feller, U., 2005. Selective transport of zinc, manganese, nickel, cobalt and cadmium in the root system and transfer to the leaves in young wheat plants. Annals of Botany 96, 425-434.

Parker, L., Kemp, P.D., Loganathan, P., West, D.M., Anderson, C.W.N., Kenyon, P.R., Morris, S.T., 2008. Effect of chicory and plantain on cadmium levels in lambs. XXI International Grassland Congress and VIII International Rangeland Congress, p. 454.

Pelletier, S., Simpson, R., Randall, P., Belanger, G., Tremblay, G.F., Seguin, P., Drapeau, R., Allard, G., 2007. Dietary cation–anion difference and cadmium concentration in grasses fertilized with chloride. Grass and Forage Science 62, 416-428.

Petering, D.H., Fowler, B.A., 1986. Discussion summary. Roles of metallothionein and related proteins in metabolism and toxicity: problems and perspectives. Environmental Health Perspectives 65, 217-224.

Ponnamperuma, F.N., 1972. The chemistry of submerged soils. Advances in Agronomy 24, 29-96.

Powell, A.M., Kemp, P.D., Jaya, I.K.D., Osborne, M.A., 2007. Establishment, growth and development of plantain and chicory under grazing. Proceedings of the New Zealand Grassland Association 69, Wairakei, New Zealand, pp. 41-45.

Reid, R.J., Dunbar, K.R., McLaughlin, M.J., 2003. Cadmium loading into potato tubers: the roles of the periderm, xylem and phloem. Plant, Cell and Environment 26, 201-206.

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.

Reuss, J.O., Dooley, H.L., Griffis, W., 1978. Uptake of cadmium from phosphate fertilizers by peas, radishes, and lettuce. Journal of Environmental Quality 7, 128-133.

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., 2005. A cadmium balance model for New Zealand pastoral systems. Unpublished report prepared for the New Zealand Fertiliser Manufacturer's Research Association. AgResearch. Hamilton.

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.

Rodrigues, S.M., Pereira, M.E., Duarte, A.C., Römkens, P.F.A.M., 2012. Soil-plant-animal transfer models to improve soil protection guidelines: A case study from Portugal. Environment International 39, 27-37.

Rothbaum, H.P., Goguel, R.L., Johnston, A.E., Mattingly, G.E.G., 1986. Cadmium accumulation in soils from long-continued applications of superphosphate. Journal of Soil Science 37, 99-107.

Rounce, J.R., Grace, N.D., Lee, J., 1997. Accumulation of cadmium in kidney and liver tissue of the suckling Romney lamb from parturition to early weaning. Proceedings of the New Zealand Society of Animal Production, 57, pp. 137-138.

Rounce, J.R., Lee, J., Treloar, B.P., Grace, N.D., 1995. Metabolic changes of cadmium and zinc in kidney and liver tissue during foetal development in Romney and Merino sheep. Proceedings of the New Zealand Society of Animal Production, 55, pp. 176-178.

Russo, S.O., Hanania, G.I.H., 1987. Buffer capacity: An undergraduate laboratory experiment. Journal of Chemical Education 64, 817-819.

Rys, G.J., 2011. A national Cadmium Management Strategy for New Zealand agriculture In: Currie, L.D., Christensen, C.L. (Eds.), Adding to the Knowledge Base for the Nutrient Manager. Occasional Report No. 24. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand.

Saggar, S., Hedley, M.J., Bolan, N.S., Gregg, P.E.H., Gillingham, A.G., Rowarth, J.S., Richardson, S., 1990a. Predicting the fate of fertiliser sulphur in grazed hill country pastures by modelling the transfer and accumulation of soil phosphorus. New Zealand Journal of Agricultural Research 33, 129-138.

Saggar, S., Hedley, M.J., Mackay, A.D., Lambert, M.G., Clark, D.A., 1990b. A nutrient-transfer model to explain the fate of phosphorus and sulphur in a grazed hill-country pasture. Agriculture, Ecosystems and Environment 30, 295-315.

Salmanzadeh, M., Balks, M.R., Hartland, A., Schipper, L.A., 2016a. Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history. Geoderma Regional 7, 271-278.

Salmanzadeh, M., Hartland, A., Stirling, C., Balks, M., Schipper, L., George, E., 2016b. Use of cadmium isotopes to distinguish sources of cadmium in New Zealand agricultural soils: preliminary results. In: Currie, L.D., Singh, R. (Eds.), *Integrated nutrient and water management for sustainable farming.* Occasional Report No. 29. http://flrc.massey.ac.nz/publications.html. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, p. 4.

Satarug, S., Moore, M.R., 2012. Emerging Roles of Cadmium and Heme Oxygenase in Type-2 Diabetes and Cancer Susceptibility. The Tohoku Journal of Experimental Medicine 228, 267-288.

Scales, G.H., 1993. Carcass fatness in lambs grazing various forages at different rates of liveweight gain. New Zealand Journal of Agricultural Research 36, 243-251.

Schipper, L.A., Sparling, G.P., Fisk, L.M., Dodd, M.B., Power, I.L., Littler, R.A., 2011. Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. Agriculture, Ecosystems and Environment 144, 95-101.

Sękara, A., Poniedziałek, M., Ciura, J., Jędrszczyk, E., 2005. Cadmium and lead accumulation and distribution in the organs of nine crops: Implications for phytoremediation. Polish Journal of Environmental Studies 14, 509-516.

Serrano, S., O'Day, P.A., Vlassopoulos, D., Garcia-Gonzalez, M.T., Garrido, F., 2009. A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. Geochimica et Cosmochimica Acta 73, 543-558.

Sharma, R.P., Street, J.C., Shupe, J.L., Bourcier, D.R., 1982. Accumulation and depletion of cadmium and lead in tissues and milk of lactating cows fed small amounts of these metals. Journal of Dairy Science 65, 972-979.

Simmler, M., Ciadamidaro, L., Schulin, R., Madejon, P., Reiser, R., Clucas, L., Weber, P., Robinson, B., 2013. Lignite reduces the solubility and plant uptake of cadmium in pasturelands. Environmental science & technology 47, 4497-4504.

Simon, L., Martin, H.W., Adriano, D.C., 1996. Chicory (*Cichorium intybus* L.) and dandelion (*Taraxacum officinale* Web.) as phytoindicators of cadmium contamination. Water, Air, and Soil Pollution 91, 351-362.

Singh, S.P., Nayyar, V.K., 1990. Accumulation characteristics of cadmium and its upper critical levels in selected vegetable species. International Journal of Environmental Studies 36, 199-204.

Smilde, K.W., Van Luit, B., Van Driel, W., 1992. The extraction by soil and absorption by plants of applied zinc and cadmium. Plant and Soil 143, 233-238.

Smolders, E., 2013. Revisiting and updating the effect of phosphorus fertilisers on cadmium accumulation in European agricultural soils. International Fertiliser Society Conference, Proceedings 724, Windsor, UK, p. 31.

Smolders, E., Mertens, J., 2012. Cadmium. In: Alloway, B.J. (Ed.), Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Springer, Dordrecht, The Netherlands, pp. 283-311.

Solly, S.R.B., Revfeim, K.J.A., Finch, G.D., 1981. Concentrations of cadmium, copper, selenium, zinc, and lead in tissues of New Zealand cattle, pigs, and sheep. New Zealand Journal of Science 24, 81-87.

Somasiri, S.C., Kenyon, P.R., Kemp, P.D., Morel, P.C.H., Morris, S.T., 2015. Growth performance and carcass characteristics of lambs grazing forage mixes inclusive of plantain (*Plantago lanceolata* L.) and chicory (*Cichorium intybus* L.). Small Ruminant Research 127, 20-27.

Sparrow, L.A., Chapman, K.S.R., Parsley, D., Hardman, P.R., Cullen, B., 1992. Response of potatoes (*Solanum tuberosum* cv. Russet Burbank) to band-placed and broadcast high cadmium phosphorus fertiliser on heavily cropped krasnozems in north-western Tasmania. Australian Journal of Experimental Agriculture 32, 113-119.

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., 1993a. 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.

Sparrow, L.A., Salardini, A.A., Bishop, A.C., 1993b. Field studies of cadmium in potatoes (*Solanum tuberosum* L.). II. Response of cvv. Russet Burbank and Kennebec to two double

superphosphates of different cadmium concentration. Australian Journal of Agricultural Research 44, 855-861.

Sparrow, L.A., Salardini, A.A., Johnstone, J., 1994. Field studies of cadmium in potatoes (*Solanum tuberosum* L.). III. Response of cv. Russet Burbank to sources of banded potassium. Australian Journal of Agricultural Research 45, 243-249.

Sparrow, L.A., Uren, N.C., 2014. Manganese oxidation and reduction in soils: Effects of temperature, water potential, pH and their interactions. Soil Research 52, 483-494.

Sposito, G., 1984. The surface chemistry of soils. Oxford University Press, New York, USA. 234 p.

Spurgeon, D.J., Hopkin, S.P., Jones, D.T., 1994. Effects of cadmium, copper, lead and zinc on growth, reproduction and survival of the earthworm *Eisenia fetida* (Savigny): Assessing the environmental impact of point-source metal contamination in terrestrial ecosystems. Environmental Pollution 84, 123-130.

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.

StatsNZ, 2013. 2012 Agricultural Census tables. Statistics New Zealand Tatauranga Aotearoa. Wellington, New Zealand. http://www.stats.govt.nz/browse_for_stats/industry_sectors/agriculture-horticulture-forestry/2012-agricultural-census-tables.aspx#.

Sun, B., Hallett, P.D., Caul, S., Daniell, T.J., Hopkins, D.W., 2011. Distribution of soil carbon and microbial biomass in arable soils under different tillage regimes. Plant & Soil 338, 17-25.

Tan, K.H., 2005. Soil sampling, preparation, and analysis. 2nd Edition. Taylor & Francis, 2005, Boca Raton, Florida, USA. 623 p.

Tanaka, K., Fujimaki, S., Fujiwara, T., Yoneyama, T., Hayashi, H., 2007. Quantitative estimation of the contribution of the phloem in cadmium transport to grains in rice plants (*Oryza sativa* L.). Soil Science and Plant Nutrition 53, 72-77.

Taylor, M., Gibb, R., Willoughby, J., Hewitt, A., Arnold, G., 2007. Soil maps of cadmium in New Zealand. Contract Report for Ministry of Agriculture and Forestry. Landcare Research. Hamilton, New Zealand. 55 p. http://maxa.maf.govt.nz/mafnet/rural-nz/sustainable-resource-use/land-management/cadmium-in-nz/soil-maps.pdf.

Taylor, M.D., 1997. Accumulation of cadmium derived from fertilisers in New Zealand soils. The Science Of The Total Environment 208, 123-126.

Taylor, M.D., Percival, H.J., 2001. Cadmium in soil solutions from a transect of soils away from a fertiliser bin. Environmental Pollution 113, 35-40.

Tiller, K.G., 1989. Heavy metals in soils and their environmental significance. Advances in Soil Science 9, 113-142.

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.

Treasury, 2016. New Zealand Economic and Financial Overview 2016. The Treasury. Wellington, New Zealand. 52 p. http://www.treasury.govt.nz/economy/overview/2016.

Tukey, J.W., 1977. Exploratory data analysis. Addison-Wesley, Reading, Pennsylvania.

Uraguchi, S., Mori, S., Kuramata, M., Kawasaki, A., Arao, T., Ishikawa, S., 2009. Root-to-shoot Cd translocation via the xylem is the major process determining shoot and grain cadmium accumulation in rice. Journal of Experimental Botany 60, 2677-2688.

Van Bruwaene, R., Kirchmann, R., Impens, R., 1984. Cadmium contamination in agriculture and zootechnology. Cellular and Molecular Life Sciences 40, 43-52.

Vannoort, R.W., Thomson, B.M., 2011. 2009 New Zealand total diet study. Agricultural compound residues, selected contaminant and nutrient elements. New Zealand Food

Safety Authority. Wellington, New Zealand. http://www.foodsafety.govt.nz/elibrary/industry/total-diet-study.pdf.

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.

Viscarra Rossel, R.A., 2008. ParLeS: Software for chemometric analysis of spectroscopic data. Chemometrics and Intelligent Laboratory Systems 90, 72-83.

Wallin, M., Sallsten, G., Fabricius-Lagging, E., Öhrn, C., Lundh, T., Barregard, L., 2013. Kidney cadmium levels and associations with urinary calcium and bone mineral density: a cross-sectional study in Sweden. Environmental Health 12, 22. www.ehjournal.net/content/12/21/22.

Warne, M., 2011. Review of, and recommendations for, the proposed New Zealand Cadmium Management Strategy and Tiered Fertiliser Management System. MAF Technical Paper No: 2011/03. Ministry of Agriculture and Forestry. Wellington, New Zealand. 34 p. http://www.mpi.govt.nz/news-resources/publications.aspx?title=Cadmium.

Watkinson, J., Lee, A., 1994. Kinetics of field oxidation of elemental sulfur in New Zealand pastoral soils and the effects of soil temperature and moisture. Nutrient Cycling in Agroecosystems 37, 59-68.

Weeks, C.A., Brown, S.N., Vazquez, I., Thomas, K., Baxter, M., Warriss, P.D., G., K.T., 2007. Multi-element survey of allotment produce and soil in the UK. Food Additives and Contaminants 24, 877-885.

Wei, S., Clark, G., Doronila, A.I., Jin, J., Monsant, A.C., 2013. Cd hyperaccumulative characteristics of Australia ecotype *Solanum nigrum L.* and its implication in screening hyperaccumulator. International Journal of Phytoremediation 15, 199-205.

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.

Welch, R.M., Shuman, L., 1995. Micronutrient nutrition of plants. Critical Reviews in Plant Sciences 14, 49-82.

Wheeler, D.M., 1997. Temporal changes in some soil chemical properties at four depths following the surface application of lime. New Zealand Journal of Agricultural Research 40, 309–316.

Wheeler, D.M., O'Connor, M.B., 1998. Why do pastures respond to lime?. Proceedings of the New Zealand Grassland Association 60, Nelson, New Zealand, pp. 57-61.

Wiersma, D., van Goor, B.J., van der Veen, N.G., 1986. Cadmium, lead, mercury and arsenic concentrations in crops and corresponding soils in the Netherlands. Journal of Agricultural and Food Chemistry 34, 1067-1074.

Williams, C.H., David, D.J., 1973. The effect of superphosphate on the cadmium content of soils and plants. Australian Journal of Soil Research 11, 43-56.

Williams, C.H., David, D.J., 1976. The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. Soil Science 121, 86-93.

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.

Wilson, D.R., Reid, J.B., Zyskowski, R.F., Maley, S., Pearson, A.J., Armstrong, S.D., Catto, W.D., Stafford, A.D., 2006. Forecasting fertiliser requirements of forage brassica crops. Proceedings of the New Zealand Grasslands Association 68, Dunedin, New Zealand, pp. 205-210.

Yamane, I., Sato, K., 1967. Effect of temperature on the decomposition of organic substances in flooded soil. Soil Science and Plant Nutrition 13, 94-100.

Yang, W., Zhang, T., Li, S., Ni, W., 2014. Metal removal from and microbial property improvement of a multiple heavy metals contaminated soil by phytoextraction with a

cadmium hyperaccumulator *Sedum alfredii H*. Journal of Soils and Sediments 14, 1385-1396.

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.

Zanders, J.M., Hedley, M.J., Palmer, A.S., Tillman, R.W., Lee, J., 1999. The source and distribution of cadmium in soils on a regularly fertilised hill-country farm. Australian Journal of Soil Research 37, 667-678.

Zhang, C., Ge, Y., Yao, H., Chen, X., Hu, M., 2012. Iron oxidation-reduction and its impacts on cadmium bioavailability in paddy soils: a review. Frontiers of Environmental Science & Engineering 6, 509-517.

Zhao, Z.Q., Zhu, Y.G., Lib, H.Y., Smith, S.E., Smith, F.A., 2003. Effects of forms and rates of potassium fertilizers on cadmium uptake by two cultivars of spring wheat (*Triticum aestivum*, L.). Environment International 29, 973-978.

Zheng, S., Zheng, X., Chen, C., 2013. Transformation of metal speciation in purple soil as affected by waterlogging. International Journal of Environmental Science & Technology 10, 351-358.

APPENDIX 1 : Soil profile descriptions

A1.1 Waikato farm

A1.1.1 Kereone silt loam (Ke)

NZSC:	Typic Orthic Allophanic
Drainage class:	Well drained
Slope:	3°
Aspect:	235°

Depth (mm)	Classification	Description
0-220	Ap	Very dark brown (7.5YR 3/2); silt loam; very friable; non sticky and slightly plastic; strongly developed medium granular and coarse crumb structure; many fine roots; gradual smooth boundary.
220-300	ABw	60% brown (7.5YR 4/2), 40% yellowish brown (10YR 5/6); silt loam; very friable; non sticky and slightly plastic; moderately developed medium granular and strongly developed medium crumb structure; common fine roots; smooth gradual boundary.
300-620	Bw	Yellowish brown (10YR 5/6); silt loam; friable; non sticky and slightly plastic; moderately developed coarse crumb and medium nut structure; common fine roots; smooth gradual boundary.
620-1100+	Bw2	Yellowish brown (10YR 5/5); silty clay loam; firm; slightly sticky and slightly plastic; moderately developed medium crumb and weakly developed medium nut structure; few fine roots.

A1.1.2 Topehaehae sandy clay loam (T)

NZSC:	Typic Recent Gley
Drainage class:	Poorly drained
Slope:	2°
Aspect:	272°

Depth (mm)	Classification	Description
0-190	Apg	Dark greyish brown (10YR 4/2); silty clay loam; friable; sticky and plastic; moderately developed fine to medium block and medium crumb structure; many fine roots; smooth gradational boundary.
190-310	ABgc	60% greyish brown (10YR 5/2), 40% yellowish brown (10YR 5/6); silt loam; very friable; non sticky and slightly plastic; moderately developed medium granular and strongly developed medium crumb structure; common fine roots; smooth gradual boundary.
310-770	Br	Light grey (2.5Y 7/1-7/2) with a few strong brown (7.5YR 5/6) coarse distinct mottles; sandy loam; firm; sticky and slightly plastic; weakly developed coarse blocky structure; no visible roots; smooth gradational boundary.
770-1100+	Cr	Light grey (2.5Y 7/1) with 10% reddish yellow (7.5YR 4/6) - dark brown (7.5YR 3/4) coarse distinct mottles; sandy loam; loose and wet; non-sticky and non-plastic; structureless; no roots; a few small twigs.

A1.1.3 Pakarau silt loam (P)

NZSC:	Typic Orthic Allophanic
Drainage class:	Moderately well drained
Slope:	4°
Aspect:	265°

Depth (mm)	Classification	Description
0-200	Ap	Very dark brown (7.5YR 3/2); silt loam; very friable; non sticky and slightly plastic; strongly developed medium granular and coarse crumb structure; many fine roots; gradual smooth boundary.
200-280	ABw	50% dark greyish brown (7.5YR 4/2), 50% yellowish brown (10YR 5/6) medium distinct worm mottles; silt loam; friable; non sticky and slightly plastic; moderately developed medium granular and strongly developed medium crumb structure; common fine roots; smooth gradual boundary.
280-600	Bw	Brownish yellow (10YR 6/6) with a few bright brown (7.5YR 5/8) medium distinct mottles; silty clay loam; friable-firm; non sticky and slightly plastic; moderately developed coarse crumb and medium nut structure; common fine roots; smooth gradual boundary.
600-840	Bg	60% Brownish yellow (10YR 6.6), 20% bright brown-yellowish red (7.5YR 5/8-5YR 4/6), 20% light grey (10 YR 7/2) coarse distinct mottles; silty clay loam; firm; sticky and plastic; moderately developed medium block structure; a few fine roots; gradual boundary.
840-1100+	BCr	Light grey (2.5Y 7/2) with 20% reddish yellow (7.5YR 4/6) – dark brown (7.5YR 3/4) coarse distinct mottles; sandy clay loam; deformable and wet; slightly sticky and slightly plastic; weak coarse block structure; no roots.

A1.1.4 Morrinsville clay loam (M)

NZSC:	Typic Orthic Granular
Drainage class:	Moderately well drained
Slope:	3°
Aspect:	340°

Depth (mm)	Classification	Description
0-180	Ap	Dark brown (7.5YR 3/2); silty clay loam; friable; sticky and plastic; strong medium granular and moderate fine nut structure; abundant fine roots; smooth gradational boundary.
180-250	ABw	60% Dark brown (7.5YR 3/3) 40% brown (7.5YR 4/3) coarse distinct mottles; clay loam; friable; sticky and plastic; moderately developed medium nut and granular structure; many fine roots; smooth gradational boundary.
250-560	Bt1	Brown (7.5YR 4/4) clay loam; firm; sticky and plastic; moderately developed medium blocky structure; common fine roots between peds; smooth gradational boundary.
560-1100+	Btg	Brown (7.5YR 5/4) with 5% pale brown (10YR 6/3) medium distinct mottles; clay loam; firm; sticky and plastic; weakly developed coarse blocky structure; few fine roots between peds.

A1.1.5 Tauwhare hill soil (Tw)

NZSC:	Mottled Orthic Recent
Drainage class:	Imperfectly to poorly drained
Slope:	15^{o}
Aspect:	185^{o}

Depth (mm)	Classification	Description
0-170	Ap	Very dark greyish brown (10YR 3/2); sandy loam; friable; slightly sticky and slightly plastic; moderately developed medium crumb and fine nut structure; abundant fine roots; smooth gradational boundary.
170-330	ABg	Dark greyish brown (10YR 4/2) with 5% 10YR 6/2 worm mottles; sandy loam; friable; slightly sticky and slightly plastic; moderately developed medium crumb and fine nut structure; many fine roots.
330-800	Bg	70% light brownish grey (10YR 6/2), 20% bright brown (7.5YR 5/8) 10% dark brownish grey (10YR 4/2) coarse prominent mottles; sandy loam; firm; sticky and plastic; moderately developed medium block structure; few fine roots; gradational boundary.
800-1100+	BR	Weathered ignimbrite, colours largely as above; firm; slightly sticky and slightly plastic; weak coarse block structure; no roots; partly moderately indurated.

A1.2 Canterbury farm

A1.2.1 Wakanui silt loam over fine sandy loam (Wk1)

NZSC:	Mottled Immature Pallic
Drainage class:	Imperfectly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-300	Ap	Dark greyish brown (10YR 4/2) with a few rusty coloured (7.5YR 5/6) coatings on root channels; silt loam; friable-firm (somewhat compacted); slightly sticky and plastic; clods and moderate medium blocky structure; abundant fine roots; gradational boundary.
300-350	ABg	Dark greyish brown (10YR 4/2) and pale brown (10YR 6/3) worm mottled silt loam; friable; slightly sticky and plastic; moderately developed fine block and coarse crumb structure; many fine roots; gradational boundary.
350-550	Bg1	Light yellowish brown (10YR 6/3) 90%, strong brown (7.5YR 6/8) 5%, dark greenish grey (5BG 5/1) 5% coarse distinct mottles; silt loam; firm; sticky and plastic; weakly develop medium block structure; few fine roots; gradational boundary.
550-960	Bg2	Light olive brown (2.5Y 6/3) 90%, strong brown (7.5YR 6/8) 5%, dark greenish grey (5BG 5/1) 5% coarse distinct mottles; fine sandy loam; friable; slightly sticky and slightly plastic; weakly develop medium block structure; few fine roots; gradational boundary.
960-1100+	Cg	Light brownish grey (10YR 6/2) 80%, strong brown (7.5YR 6/8) 10%, dark greenish grey (5BG 5/1) 10% coarse distinct mottles; few flecks of purplish black organic matter; silty clay loam; firm; sticky and plastic; massive; no roots.

A1.2.2 Wakanui silt loam on silty clay loam (Wk2)

NZSC:	Mottled Immature Pallic
Drainage class:	Imperfectly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-280	Ap	Dark greyish brown (10YR 4/2) with common bright brown (7.5YR 5/8) coatings on root channels; silt loam; firm (compacted); slightly sticky and plastic; clods and moderate medium blocky structure; abundant fine roots; gradational boundary.
280-350	ABg	Dark greyish brown (10YR 4/2) 50% and pale brown (10YR 6/3) 50% worm mottled silt loam; friable; slightly sticky and plastic; moderately developed fine block and coarse crumb structure; many fine roots; gradational boundary.
350-650	Bg1	Light yellowish brown (2.5Y 6/4) 70%, light brownish grey (2.5Y 6/2) 15%; bright brown (7.5YR 5/8) 15% coarse distinct mottles; silt loam; firm; sticky and plastic; weakly develop medium block structure; few fine roots; gradational boundary.
650-850	Bg2	Light olive brown (2.5Y 6/3) 80%, strong brown (7.5YR 6/8) 5%, grey (2.5Y 6/1) 15% coarse distinct mottles; silty clay loam; firm; sticky and plastic; weakly develop medium block structure; few fine roots; gradational boundary.
850-1100+	Cg	Grey-light brownish grey (2.5Y 6/1-6/2) 70%, bright brown (7.5YR 5/8) 30% coarse distinct mottles; fine sandy loam; firm; slightly sticky and slightly plastic; structureless; no roots; very wet.

A1.2.3 Wakanui fine sandy loam (Wk3)

NZSC:	Mottled Immature Pallic
Drainage class:	Imperfectly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-250	Ap	Dark greyish brown (10YR 4/2) with a few bright brown (7.5YR 5/8) coatings on root channels; fine sandy loam; friable; non sticky and slightly plastic; moderate coarse crumb and medium blocky structure; abundant fine roots; gradational boundary.
250-310	ABg	Dark greyish brown (10YR 4/2) 50% and pale brown (10YR 6/3) 50% worm mottled fine sandy loam; friable; slightly sticky and slightly plastic; moderately developed medium nut and coarse crumb structure; many fine roots; gradational boundary.
310-460	Bw1	Yellowish brown (10YR 5/4) with a few light brownish grey (2.5Y 6/2) and bright brown (7.5YR 5/8) medium distinct mottles; fine sandy loam; friable; slightly sticky and slightly plastic; moderately developed medium nut and coarse crumb structure; common fine roots; gradational boundary.
460-750	Bw2	Brown (10YR 5/3) 80%, light brownish grey (2.5Y 6/2) 10%, bright brown (7.5YR 5/8) 10% coarse distinct mottles; loamy sand with a few scattered greywacke pebbles near the base; friable; non sticky and non plastic; weak medium crumb structure; a few fine roots; sharp boundary.
750-1000+	2C	Weakly weathered greywacke gravels in a coarse sand matrix.

A1.2.4 Temuka silty clay loam (Tm1)

NZSC:	Typic Orthic Gley
Drainage class:	Poorly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-280	Apg	Dark brown (7.5YR 3/2) silty clay loam; friable-firm because of compaction; slightly sticky and plastic; moderately developed medium granule and fine nut structure; abundant fine roots; gradational boundary.
280-360	ABg	Dark brown (7.5YR 3/2) and dark greyish brown (10YR 4/2) worm mottled silty clay loam; moderately firm; sticky and plastic; moderately developed fine nut and block structure; many fine roots; gradational boundary.
360-550	Bg	Greyish brown (10YR 5/2) silty clay loam; firm; sticky and plastic; weakly developed medium block structure; common fine roots; gradational boundary.
550-820	Br	Dark greyish brown (10YR 4/2) with a few strong brown (7.5YR 4/6 stains and mottles; peaty silty clay loam; firm; deformable; sticky and plastic; weakly developed prismatic and medium blocky structure; few roots; a few fragments of wood/ twigs and leaves; gradational boundary.
820-1100+	Cr	Greenish grey (5GY 5/1); silt loam; slightly sticky and plastic; structureless; no roots.

A1.2.5 Temuka silty clay loam over peaty loam (Tm2)

NZSC:	Typic Orthic Gley
Drainage class:	Poorly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-280	Apg	Very dark brown (10YR 3/2) silty clay loam; friable-firm because of compaction; slightly sticky and plastic; moderately developed medium granule and fine nut structure; abundant fine roots; gradational boundary.
280-340	ABg	Very dark brown (10YR 3/2) and dark greyish brown (10YR 4/2) worm mottled silty clay loam; moderately firm; sticky and plastic; moderately developed fine nut and block structure; many fine roots; gradational boundary.
340-650	Bg	Grey to olive grey (5Y 5/1- 5/2) 90%, bright brown (7.5YR 5/8) 10%, coarse distinct mottles; silty clay loam; firm; sticky and plastic; weakly developed medium block structure; common fine roots; gradational boundary.
650-900	Br	Dark grey (5Y 4/1) with a few (<2%) bright brown coarse distinct mottles and stains; silty clay loam; slightly peaty; deformable; sticky and plastic; weakly developed coarse block structure; a few fine roots; gradational boundary.
900-1100+	Om	Very dark greyish brown (2.5Y 3/2) peaty loam with common fragments of vegetation; deformable; sticky and plastic; structureless; no roots.

A1.2.6 Waimairi peaty loam (Wm1)

NZSC:	Peaty Orthic Gley
Drainage class:	Poorly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-330	Apg	Dark greyish brown (10YR 4/2) peaty silty clay loam; friable; slightly sticky and plastic; moderately developed fine-medium nut and coarse crumb structure; abundant fine roots; gradational boundary.
330-440	ABg	Dark greyish brown (10YR 4/2) 60% and light brownish grey (2.5Y 6/2) 40%, medium distinct mottles; silty clay loam; friable; slightly sticky and plastic; moderately developed fine-medium blocky structure; abundant fine roots; sharp wavy boundary.
440-700	Oh	Dark brown (7.5YR 3/2) loamy peat; soft; non sticky and non plastic; structureless; very wet; few fine roots; gradational boundary.
700-1100+	Cr	Dark brown (7.5YR 4/2) peaty clay; soft and deformable; sticky and plastic; structureless; a few pieces of wood and vegetation.

A1.2.7 Waimairi peaty loam on sand (Wm2)

NZSC:	Peaty Orthic Gley
Drainage class:	Poorly drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-250	Ap	Very dark greyish brown to dark brown (7.5YR 3/1) peaty loam; friable; non sticky and slightly plastic; moderately developed fine-medium nut and medium granule structure; abundant fine roots.
250-520	Br	Light brownish grey (2.5Y 6/1-6/2) with 5% bright brown (7.5YR 5/8) coarse distinct mottles; silty clay loam; deformable; sticky and plastic; moderately developed prismatic and medium block structure; common fine live roots and fragments of vegetation; sharp wavy boundary.
520-740	Cr1	Olive grey (5Y 4/2) grading down to greenish grey (5BG 4/1) peaty fine sandy loam; friable; slightly sticky and plastic; structureless; few fine roots; common fragments of vegetation and wood; sharp wavy boundary.
740-980	Cr2	Greenish grey (5GY 5/1) silty clay loam; deformable; sticky and plastic; structureless; few fine roots; common fragments of vegetation and wood; gradational boundary.
980-1100+	Cr3	Greenish grey (5GY 5/1) sandy loam; loose; non sticky and non plastic; structureless; no roots; common fragments of vegetation and wood.

A1.2.8 Templeton fine sandy loam (Te1)

NZSC:	Typic Immature Pallic
Drainage class:	Well drained
Slope:	0^{o}
Aspect:	N/A

Depth (mm)	Classification	Description
0-280	Ap	Dark greyish brown to dark brown (10YR 4/2-4/3) fine sandy loam; friable; non sticky and non plastic; moderately developed fine nut and coarse crumb structure; many fine roots; sharp wavy boundary.
280-330	ABw	Dark brown (10YR 4/3) and yellowish brown (10YR 5/4) worm mottled sandy loam; friable; non sticky and non plastic; moderately developed fine nut and coarse crumb structure; many fine roots; gradational boundary.
330-520	Bw1	Yellowish brown (10YR 5/4) with a few distinct fine strong brown (7.5YR 5/6) mottles near the base; sandy loam with a few fine greywacke pebbles; friable; non sticky and slightly plastic; weakly developed fine nut and medium crumb structure; common fine roots; gradational boundary.
520-1100+	BC	Light olive brown (2.5Y 5/4) with a few feint fine strong brown (7.5YR 5/6) mottles throughout; loamy sand with a few scattered fine rounded greywacke gravels and grit; friable; non sticky and non plastic; weakly developed medium crumb structure; few fine roots.

APPENDIX 2 : Soil pH buffer capacity analysis for field trial soils

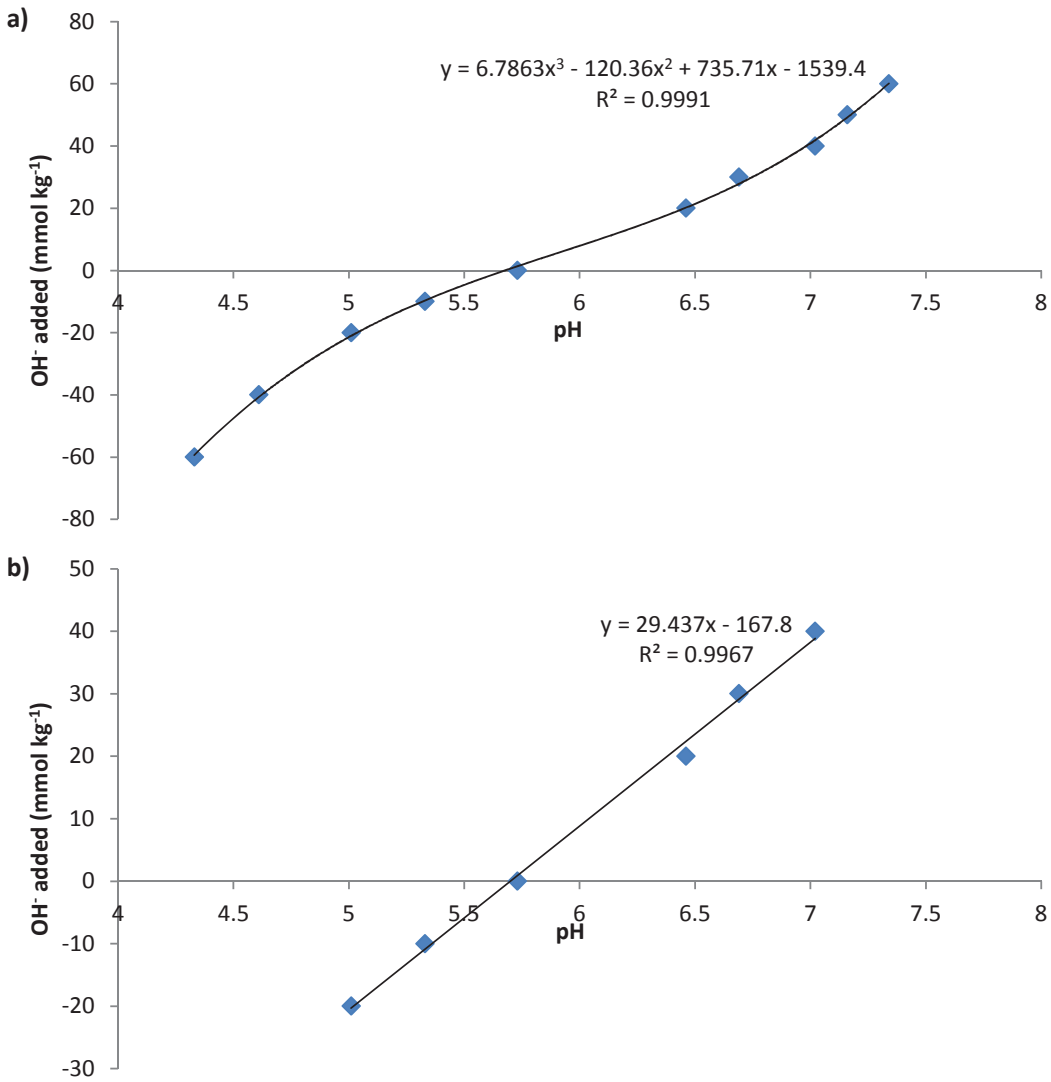

Figure A2.1. For the Kereone soil; **a)** full pH buffer curve with all data points, and **b)** data subset used to derive the soil pH buffer capacity (29.4 mmol kg^{-1} pH^{-1}).

Table A2.1. Calculation of $CaCO_3$ or elemental S requirement to shift pH by 0.5 units for the Kereone soil.

Soil pH buffer capacity (mmol kg^{-1} pH^{-1})	29.4
Soil bulk density (t m^{-3})	0.77
Soil depth (cm)	15
Mass of soil in 1 ha (t ha^{-1})	1155
Change in soil pH required (pH units)	0.5
Amount of H^+ or OH^- required (mol ha^{-1})	16979
Amount of $CaCO_3$ or Elemental S required for desired pH change (mol ha^{-1})	8489
Amount of $CaCO_3$ required for desired pH change (kg ha^{-1})	849
Amount of elemental S required for desired pH change (kg ha^{-1})	272

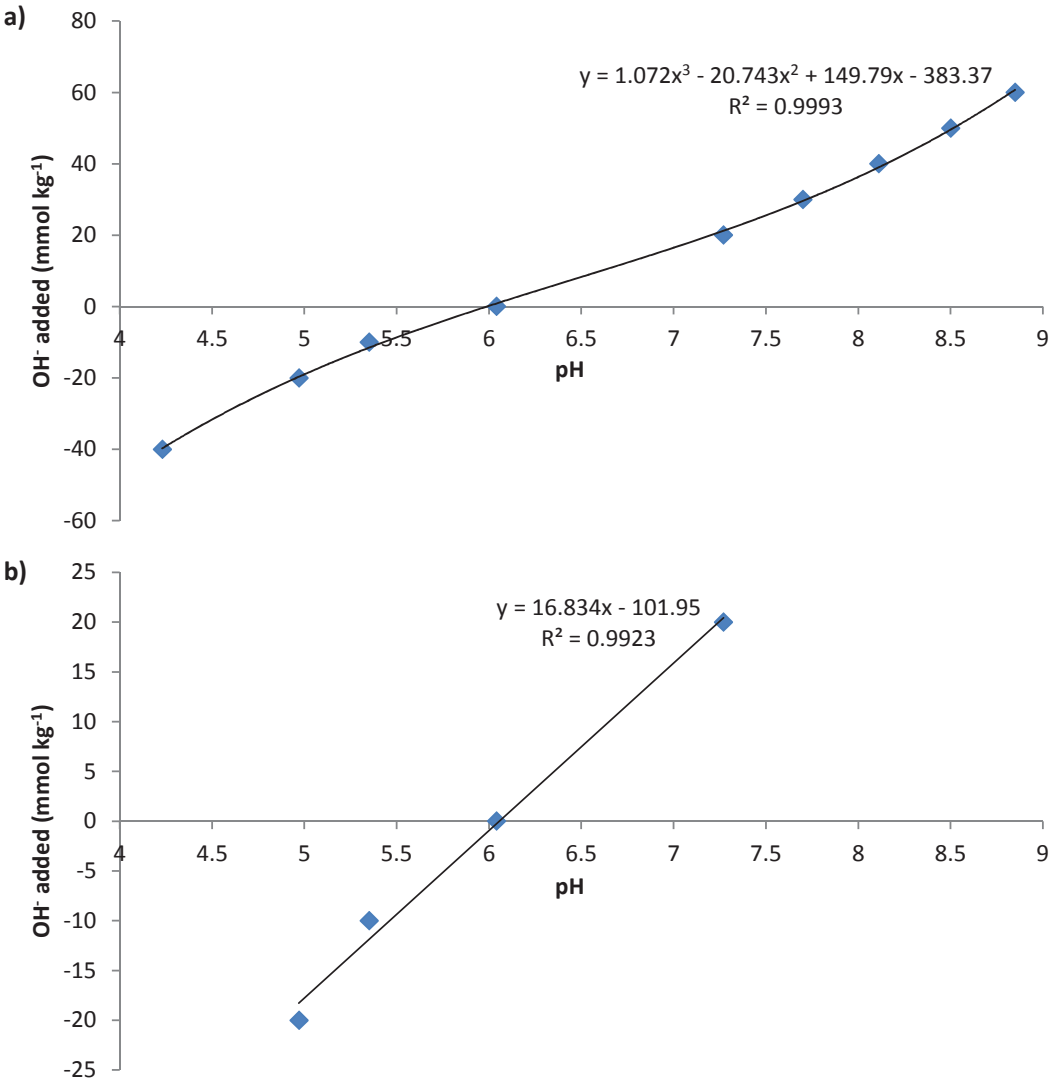

Figure A2.2. For the Topehaehae soil; **a)** full pH buffer curve with all data points, and **b)** data subset used to derive the soil pH buffer capacity (16.8 mmol kg^{-1} pH^{-1}).

Table A2.2. Calculation of $CaCO_3$ or elemental S requirement to shift pH by 0.5 units for the Topehaehae soil.

Soil pH buffer capacity (mmol kg^{-1} pH^{-1})	16.8
Soil bulk density (t m^{-3})	0.90
Soil depth (cm)	15
Mass of soil in 1 ha (t ha^{-1})	1350
Change in soil pH required (pH units)	0.5
Amount of H^+ or OH^- required (mol ha^{-1})	11363
Amount of $CaCO_3$ or Elemental S required for desired pH change (mol ha^{-1})	5681
Amount of $CaCO_3$ required for desired pH change (kg ha^{-1})	568
Amount of elemental S required for desired pH change (kg ha^{-1})	182

APPENDIX 3 : Soil pH versus soil extractable Cd concentration at the field trial midpoint

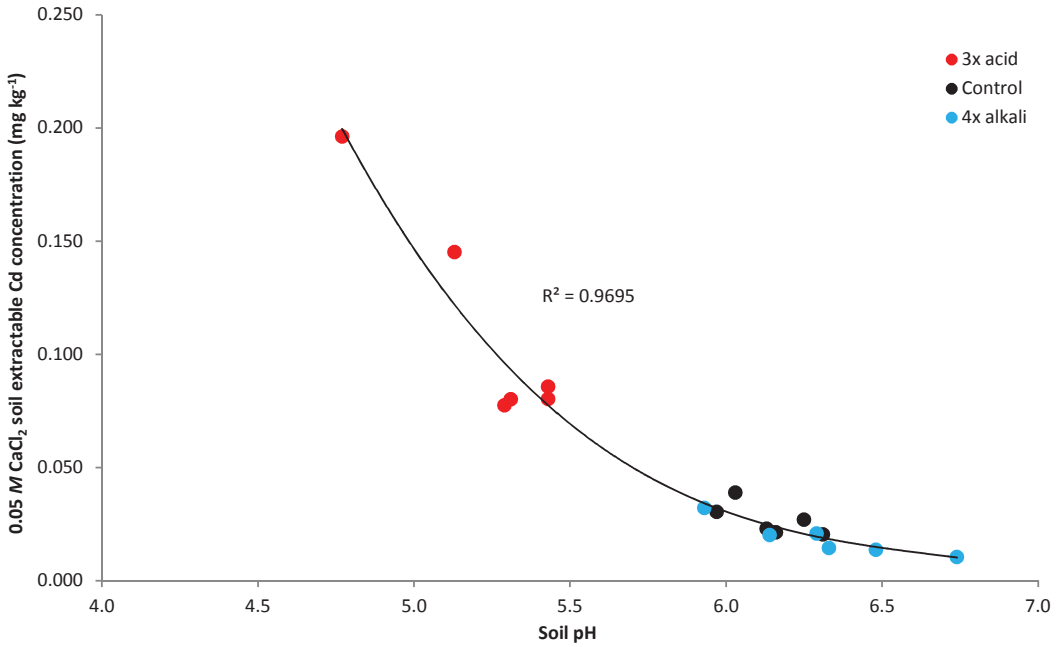

Figure A3.1. Relationship between 0.05 M $CaCl_2$ soil extractable Cd concentration and soil pH for selected treatments (ryegrass 'control', '3x acid' and '4x alkali' treatments) across both soil types at the trial mid-point soil sampling (24 November 2015).

APPENDIX 4 : Statement of contribution to Doctoral thesis containing publications

DRC 16

MASSEY UNIVERSITY
GRADUATE RESEARCH SCHOOL

STATEMENT OF CONTRIBUTION
TO DOCTORAL THESIS CONTAINING PUBLICATIONS

(To appear at the end of each thesis chapter/section/appendix submitted as an article/paper or collected as an appendix at the end of the thesis)

We, the candidate and the candidate's Principal Supervisor, certify that all co-authors have consented to their work being included in the thesis and they have accepted the candidate's contribution as indicated below in the *Statement of Originality*.

Name of Candidate: Aaron Stafford

Name/Title of Principal Supervisor: Associate Professor Chris Anderson

Name of Published Research Output and full reference:

Name: Cadmium accumulation by forage species used in New Zealand livestock grazing systems.

Full reference:
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.

In which Chapter is the Published Work: Chapter 4

Please indicate either:

- The percentage of the Published Work that was contributed by the candidate: 70%

  and / or

- Describe the contribution that the candidate has made to the Published Work:

  The pot trial that generated the data for this paper was originally carried out for another purpose (plant P use efficiency) at AgResearch. My contribution was to add additional species to those being tested, carry out the additional analysis, interrogate the data and author the resultant research paper.

Aaron Stafford Digitally signed by Aaron Stafford Date: 2017.05.28 21:12:54 +12'00'
Candidate's Signature

25 / 5 / 17
Date

Christopher Anderson Digitally signed by Christopher Anderson Date: 2017.05.28 09:28:04 +12'00'
Principal Supervisor's signature

Date

GRS Version 3– 16 September 2011