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Cadmium accumulation in agricultural soils

A thesis
submitted in fulfilment
of the requirements for the degree
of
Doctor of Philosophy in Environmental Science
at
The University of Waikato
by
MAHDIYEH SALMANZADEH

2017
Abstract

Cadmium (Cd) has accumulated in New Zealand (NZ) soils as a result of phosphate fertiliser application. Cadmium is a biotoxic heavy metal and can be adsorbed by soil and enter the human food chain. Three objectives were investigated in this thesis: 1. Determine if the distribution of Cd varies between soils with contrasting mineralogy and drainage characteristics, but the same phosphate fertiliser history, 2. Evaluate the utility of Cd stable isotope ratios ($\delta^{114/110}$Cd) to trace the sources of Cd in NZ soils through time and distinguish the contribution of different sources of Cd in NZ soils, and, 3. Determine whether there is a difference in the concentration of Cd in irrigated and unirrigated soils within the same paddock.

The concentration of Cd was measured in three soils, with contrasting mineralogy and drainage characteristics within the same paddock, and thus same fertiliser history. The mean concentration of Cd in topsoil (0-7.5 cm) samples was 0.77 mg kg$^{-1}$ (range 0.56-0.99) in the Horotiu soil (Orthic Allophanic Soil in NZ soil classification, Typic Hapludand in US soil taxonomy), 0.83 mg kg$^{-1}$ (range 0.60-1.11) in the Bruntwood soil (Impeded Allophanic Soil in NZ soil classification, Aquic Hapludand in US soil taxonomy) and 0.78 mg kg$^{-1}$ (range 0.46-0.96) in the Te Kowhai soil (Orthic Gley Soil in NZ classification, Typic Humaquept in US soil taxonomy). There were no significant differences in the concentration, and/or the total mass of Cd between the three soils. Cadmium was mainly adsorbed to the near surface soil regardless of soil mineralogy and drainage characteristics. Thus, it was concluded that it is appropriate to apply the same Cd management approach (The Tiered Fertiliser Management System) to the investigated soil types.
Isotope ratios of Cd ($\delta^{114/110}$Cd) were used to trace the sources of Cd in a long-term irrigation and fertiliser trial at Winchmore, Canterbury, New Zealand. The isotopic composition of pre-2000 fertilisers ($\delta^{114/110}$Cd = 0.10 ± 0.05 to 0.25 ± 0.04) was comparable to the Nauru source rocks used in fertiliser manufacture ($\delta^{114/110}$Cd = 0.22 ± 0.04), but distinct from the control subsoil ($\delta^{114/110}$Cd = -0.33 ± 0.04) and post-2000 fertilisers ($\delta^{114/110}$Cd range of -0.17 ± 0.03 to 0.01 ± 0.05). The isotopic compositions of fertilised soil samples ranged from $\delta^{114/110}$Cd = 0.08 ± 0.03 to $\delta^{114/110}$Cd = 0.27 ± 0.04, which were comparable to pre-2000 fertilisers. Thus, it becomes possible to distinguish the sources of Cd within the soil using isotopes. The fractional distribution of Cd sources confirmed the main contribution of Nauru-derived phosphate fertilisers (pre-2000 fertilisers) in increasing the amount of Cd in soils at the Winchmore research farm.

The concentration and distribution of Cd in adjacent irrigated and unirrigated soils with the same phosphate fertiliser history were investigated. Twenty-two pairs of soil samples from 4 depths (0-10, 10-20, 20-30 and 30-40 cm) were taken from irrigated and unirrigated areas in the same paddocks on different dairy farms from three regions of New Zealand (Bay of Plenty, Manawatu-Wanganui, and Canterbury). The mean concentration of Cd (depth of 0-10 cm and 10-20 cm) and the cumulative mass of Cd (depths of 0-20, 0-30, and 0-40 cm) were higher ($P < 0.05$) in unirrigated soil than in irrigated soil. Total Cd was about 10% less abundant in the 0-40 cm depth range in irrigated soil (mean of 0.63 kg ha$^{-1}$) than unirrigated soil (mean of 0.73 kg ha$^{-1}$), with the average difference of 7.2 g ha$^{-1}$yr$^{-1}$ for the 0-40 cm depth. The significant difference ($P < 0.05$) in the cumulative mass of Cd between irrigated and unirrigated soils demonstrated that irrigation may have
enhanced the mobility of Cd. However, overall the results demonstrate that Cd was generally immobile and mainly absorbed to the near surface of the soils studied.
Acknowledgements

My PhD journey would not have been possible without the support of supervisors, co-workers, friends and family.

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Chapter 1. Introduction

1.1 Background and significance of the study

Cadmium (Cd) is a biotoxic heavy metal that is easily absorbed by soils and plants. When Cd accumulates in soils, it can enter the human food chain via plants and grazing animals (Gray et al. 2003; Environmental Science and Monitoring Group 2007). Cadmium in New Zealand (NZ) soils comes mainly from phosphate fertiliser (Gray et al. 1999; Loganathan et al. 2003; McDowell 2012) and this has led to concern about the effect of Cd accumulation, leading to Cd being described as ‘the trace metal of greatest concern with respect to food standards in New Zealand’ (Taylor et al. 2010).

The main pathways of Cd entry into the human food chain are plants (especially leafy vegetables such as spinach) and offal (Cadmium Working Group 2008). Here, in New Zealand, kidneys from animals older than 2.5 years are not eligible for human consumption and are prohibited from export due to potential for a high content of Cd (Lee et al. 1994; Cadmium Working Group 2008).

Historical sources of phosphate fertiliser in New Zealand mainly originated from Nauru Island rock phosphate, which contains a relatively high concentration of Cd (450 mg Cd kg$^{-1}$ P). Since 1997 the main source of phosphate fertilisers has changed from Nauru Island rock phosphates to a variety of phosphate rocks with a lower concentration of Cd. At about the same time, the NZ fertiliser industry decided to produce phosphate fertilisers with a Cd concentration lower than 280 mg Cd kg$^{-1}$ P. However, some NZ soils still have elevated Cd due to historical loading, especially in parts of the Waikato region where fertilisers use has historically been high, particularly in the dairy and horticulture industries (Taylor
et al. 2007; Cadmium Working Group 2008). There is also concern about the potential for Cd to translocate through the soil profile, especially in sandy soils, and cause groundwater pollution (Rothbaum et al. 1986; McBride et al. 1997). To maintain the productivity of NZ soils, phosphate fertiliser application must continue and thus it is important to understand the processes controlling the fate of Cd in NZ soils and the wider environment, so that appropriate management strategies can be implemented.

1.2 Aim and objectives

The overall aims of this study were to assess soil Cd accumulation between contrasting soils, trace the input sources of Cd through time, and determine the potential of Cd to translocate through the soil profile in infiltration. The specific objectives of this research were:

1) To determine if the distribution of Cd varies between soils with contrasting mineralogy and drainage characteristics, but the same P fertiliser history.

2) To evaluate the utility of Cd stable isotope ratios ($^{114/110}$Cd) to trace the sources of Cd in NZ soils through time and distinguish the contribution of different sources of Cd in NZ soils.

3) To determine whether there is a difference in the concentration of Cd in irrigated and unirrigated soils within the same paddock (hence with the same phosphate fertiliser history).
1.3 Thesis structure and outline

This thesis is divided into six chapters including; Introduction (Chapter 1), Literature Review (Chapter 2), Research components (Chapters 3-5) and Conclusion (Chapter 6).

Chapter 1 is a general introduction describing Cd issues in New Zealand, the overall aims and the specific objectives to achieve those aims.

Chapter 2 is a literature review on Cd in NZ agricultural soils, the different factors affecting the accumulation of Cd in soils, Cd uptake by plants, animals, and humans, and the methods of Cd concentration and isotope measurement in soil samples.

Chapter 3 is a journal article published in Geoderma Regional detailing the results of Cd accumulation in three contrasting NZ soils with the same fertiliser history.

Chapter 4 is a journal article published in Environmental Science & Technology which details the results of a stable isotope evaluation of Cd accumulation trends at the Winchmore research farm in Canterbury, New Zealand.

Chapter 5 is a journal article published in Agriculture, Ecosystems & Environment which describes the results of Cd accumulation in irrigated and unirrigated soils of the same paddocks (therefore with the same fertiliser history).

Chapter 6 provides an overview and synthesis of the total research effort with some suggestions for further research.
References


Chapter 2. Literature review: Cadmium accumulation in agricultural soils

2.1 Introduction

Cadmium (Cd) naturally occurs at low concentrations in air, soil and water (Cadmium Working Group 2008). The average amount of Cd in the Earth’s crust is between 0.15 to 0.20 mg kg\(^{-1}\), and Cd is ranked as 64\(^{th}\) in crustal abundance of the elements (Krauskopf 1979). It is therefore a natural element found in many environmental samples (Adriano 2001). Cadmium concentration varies between different soils according to the parent material: soils derived from igneous rocks generally have the lowest amounts of Cd (< 0.10 to 0.30 mg kg\(^{-1}\)), soils from metamorphic rocks contain intermediate amounts of Cd (0.10 to 1.0 mg kg\(^{-1}\)), while soils from sedimentary rocks contain the highest amounts of Cd (0.30 to 11 mg kg\(^{-1}\)) (Adriano 2001).

The biotoxicity level of Cd in soils depends on its concentration, its bioavailability and therefore its propensity to transfer to ecosystems, or ‘bioaccumulate’ (McDowell 2010). Cadmium is poisonous to all living organisms and has cumulative effects, causing growth retardation in children, kidney disease, anaemia, osteomalacia, anosmia, cancer, itai-itai (results in painful bone demineralization because of Cd replacement of calcium) and many other adverse health effects (Mennear 1979; Yasumura et al. 1980; Ryan et al. 1982; Herber 1994; Kross et al. 1995; Jiries 2003; Mahar et al. 2015). For example, from 1922 to 1965 more than 100 human deaths occurred in Japan due to Cd poisoning (Yeung & Hsu 2005). Thus, it is desirable to minimise the amount of Cd in food stuffs.
The accumulation rate of Cd in soils is related to various factors such as the type and amount of phosphate fertilisers used, soil properties such as texture, organic matter content, acidity (pH), available micro-elements in soil such as zinc (Zn) and macro-nutrients such as phosphate (Chaney & Hornick 1978; Whitten & Ritchie 1991; He & Singh 1993; Guttormsen et al. 1995).

This literature review overviews the factors affecting Cd accumulation and adsorption onto soil surfaces, especially in agricultural soils following phosphate fertiliser application. The chemical properties of Cd and soil surface chemistry as well as the historical and current situation of Cd in NZ agricultural soils is also reviewed and different methods of Cd measurement in soil samples are described.

### 2.2 Cadmium sources in agricultural soils

The natural sources of Cd entering soils are rocks, forest fires, and volcanic emissions (Nriagu 1980a). There are three main anthropogenic sources for Cd: 1) phosphate fertilisers, 2) atmospheric deposition and 3) sewage sludge and industrial wastes applied to agricultural soils (Loganathan et al. 2003). Industrial wastes originate from activities such as mining, iron and steel production, coal combustion, oil and petrol combustion, wood combustion, waste incineration, rubber tire wear (Nriagu 1980a), and by-products of Zn bearing ore treatment (Brehler et al. 1969). Plastics (as stabiliser for polyvinyl plastics), ceramics, paints, rubber, glass, batteries, alloy manufacture, building materials, photography, lithography and engraving are other sources of Cd (Adriano 2001; Wei et al. 2010).

Despite a wide range of possible sources, the main source of Cd in NZ agricultural soils is undoubtedly phosphate fertiliser application (Loganathan et al. 2003).
Fergusson and Stewart (1992) showed that within a 20 km radius of Christchurch, the input of Cd to land from the atmosphere was 10-20% of the Cd input from fertiliser.

2.3 Cadmium and soil surface chemistry

There are six main Cd minerals in the environment: greenockite [cadmium sulfide (CdS), hexagonal], hawleyite (CdS, cubic), octavite [cadmium carbonate (CdCO$_3$)], monteponite [cadmium oxide (CdO)], cadmoselite [cadmium selenide (CdSe)] and saukovite [cadmium metacinnabar ((Hg, Cd)S), cubic] (Bewers et al. 1987). Cadmium can dissolve in most inorganic acids and is insoluble in alkaline environments. Usually Cd is found in association with Zn, lead (Pb) and Cu in the environment (Kim 2005).

2.3.1 Properties of cadmium

Cadmium, with the atomic number of 48 and atomic mass of 112.411 amu, is a soft, bluish-white metal and is chemically similar to Zn (Holleman et al. 1985). Cadmium was first reported in 1817 as an impurity in ZnCO$_3$ (Nriagu 1980a). The name of cadmium is derived from the Greek name of zinc carbonate, cadmia (Nriagu, 1980a). The oxidation state of Cd is usually +2 (Cd can also exist in the +1 state) and because of its density (8.65 g cm$^{-3}$), Cd belongs to the group of “heavy metal” elements (Zanders 1998). Cadmium is a “nonessential element” to living organisms and is known as a toxic element (Adriano 2001). Because of Cd solubility in acids (Nriagu 1980a), the acidity of agricultural soils should be considered within any assessment of the availability of Cd for plant/animal uptake.
Of the most common heavy metals, Cd has a tendency to accumulate in plants and therefore can enter the human food chain (Sherlock & Smart 1986).

2.3.2 Soil surface complexation chemistry

There are three main reactive surfaces involved in soil sorption behaviour including layer silicate clays, organic matter and metal oxides (Gray 1998). Layer silicate clays play an important role in Cd adsorption to soil (Reid & McDuffie 1981) and have permanent charge due to isomorphous substitution of ions within the clay lattice, and some variable charges sites can also be found at the fractured edges of lattices (Gray 1998). Organic matter has a net negative charge mainly because of dissociation of carboxyl and phenolic groups, and therefore the reaction between metals and soil organic matter can happen due to ion exchange, complexation, and precipitation reactions (Gray 1998). Cadmium can also adsorb to the surface of minerals such as aluminum (Al), iron (Fe) and manganese (Mn) oxides and hydroxides (Ainsworth et al. 1994). The fate and transport of Cd in soils are affected by interactions with the solid and aqueous phases of soils and therefore a complete description of Cd behaviour in the soil zone must factor in both soil surface and aqueous chemistry (Figure 2.1) (Kookana et al. 1999).
2.3.3 Different forms and amounts of cadmium in the environment including soil

The commonly occurring forms of Cd in the environment are cadmium sulfide (CdS), cadmium carbonate (CdCO₃) and cadmium oxide (CdO) (Brehler et al. 1969). Cadmium also forms some hydroxide and other inorganic complexes (e.g. CdCl₂). There are different forms of Cd in soils: free (hydrated) ions in solution, soluble inorganic and organometallic (e.g. Cd-humic) complexes, as ions adsorbed to hydrous oxides of Mn, Fe, and Al, as insoluble organometallic complexes, as solid phase insoluble precipitates such as sulfides, phosphates, and carbonates, and in solid phase minerals such as biotite and riebeckite (Peterson & Alloway 1979). The major species of Cd in soil solutions of agricultural soils is free Cd^{2+} ion or Cd complexed by inorganic ligands (Mahler
et al. 1980; Tills & Alloway 1983; Holm et al. 1993; Naidu et al. 1994; Sauvé et al. 1999). Taylor and Percival (2001) indicated that less than 1% of added Cd was present in soil solution in agricultural soils from Lower Hutt, New Zealand, and between 55% to 90% of the soluble Cd was in the form of Cd$^{2+}$, together with chloride and sulphate complexes, even when the concentrations of nitrate and phosphate were considerable (Taylor & Percival 2001). Different factors such as ion exchange, solubility, adsorption/desorption, and redox reactions affect the concentration of Cd$^{2+}$ in soil solution (Gray 1998), moreover, the concentration of Cd is different in various environmental media (Table 2.1).
## Table 2.1. Mean and range of concentrations of Cd (ppm) in various environmental materials (from Adriano 2001)*

<table>
<thead>
<tr>
<th>Material</th>
<th>Average concentration</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igneous rocks*</td>
<td>0.08</td>
<td>0.001-0.60</td>
</tr>
<tr>
<td>Metamorphic rocks*</td>
<td>0.06</td>
<td>0.005-0.87</td>
</tr>
<tr>
<td>Sedimentary rocks*</td>
<td>0.06</td>
<td>0.05-500</td>
</tr>
<tr>
<td>Recent sediments*</td>
<td>0.53</td>
<td>0.02-6.2</td>
</tr>
<tr>
<td>Crude oil b</td>
<td>0.008</td>
<td>0.0003-0.027</td>
</tr>
<tr>
<td>Coal b</td>
<td>0.10</td>
<td>0.07-0.18</td>
</tr>
<tr>
<td>Fly ash b</td>
<td>11.7</td>
<td>6.5-17</td>
</tr>
<tr>
<td>Phosphate rocks c</td>
<td>25</td>
<td>0.2-340</td>
</tr>
<tr>
<td>Phosphate fertilisers (mixed) d</td>
<td>4.3</td>
<td>1.5-9.7</td>
</tr>
<tr>
<td>Soil f (world non-polluted) f</td>
<td>0.35</td>
<td>0.01-2.0</td>
</tr>
<tr>
<td>Fertilised rural soils in Australia e</td>
<td>0.42</td>
<td>0.01-13.9</td>
</tr>
<tr>
<td>Unfertilised soils of Australia e</td>
<td>0.37</td>
<td>0.01-12.02</td>
</tr>
<tr>
<td>National arable of U.S. soils (n=3202)g</td>
<td>0.255</td>
<td>0.03-0.94</td>
</tr>
<tr>
<td>U.S. fruits (n = 190) h</td>
<td>0.005</td>
<td>0.0043-0.012</td>
</tr>
<tr>
<td>U.S. vegetables (n=1891) h</td>
<td>0.028</td>
<td>0.016-0.13</td>
</tr>
<tr>
<td>U.S. crop grains (n = 1302) h</td>
<td>0.047</td>
<td>0.014-0.21</td>
</tr>
<tr>
<td>U.S. field crops (n =2858) h</td>
<td>0.21</td>
<td>&lt;0.001-3.80</td>
</tr>
<tr>
<td>Polluted river sediments i</td>
<td>---</td>
<td>30 - &gt;800</td>
</tr>
<tr>
<td>Unpolluted sediments i</td>
<td>---</td>
<td>0.04-0.8</td>
</tr>
<tr>
<td>Grasses i</td>
<td>---</td>
<td>0.03-0.3</td>
</tr>
<tr>
<td>Ferns f</td>
<td>0.13</td>
<td>---</td>
</tr>
<tr>
<td>Mosses i</td>
<td>---</td>
<td>0.7-1.2</td>
</tr>
<tr>
<td>Lichens i</td>
<td>---</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>Leaves of deciduous trees i</td>
<td>---</td>
<td>0.1-2.4</td>
</tr>
<tr>
<td>Branches of deciduous trees i</td>
<td>---</td>
<td>0.1-1.3</td>
</tr>
<tr>
<td>Leaves of coniferous i</td>
<td>---</td>
<td>0.1-0.9</td>
</tr>
<tr>
<td>Freshwater f</td>
<td>0.10*</td>
<td>0.01-3</td>
</tr>
<tr>
<td>Seawater f</td>
<td>0.11*</td>
<td>&lt;0.01-9.4</td>
</tr>
<tr>
<td>Oysters i</td>
<td>---</td>
<td>&lt;1-12 (DW**)</td>
</tr>
<tr>
<td>Fish muscle (fillet) i</td>
<td>---</td>
<td>&lt;0.01 (DW)</td>
</tr>
<tr>
<td>Fish organs i</td>
<td>---</td>
<td>2-20 (DW)</td>
</tr>
<tr>
<td>Mussels (polluted freshwater) i</td>
<td>---</td>
<td>≤3 (DW)</td>
</tr>
<tr>
<td>Cigarettes i</td>
<td>---</td>
<td>&lt;0.5-3 (DW)</td>
</tr>
</tbody>
</table>
| Kidneys (exposed persons) i           | ---                   | Up to 500 (WW***)
| Kidneys (smokers) i                   | ---                   | ≤6 (WW)     |
| Kidneys (nonsmokers) i                | ---                   | ≤3 (WW)     |
| Liver (human) i                       | ---                   | 0.1-3 (WW)  |
| Lung tissue (unexposed) i             | ---                   | ≤0.1 (WW)   |
| Bones (human) i                       | ---                   | < 0.01 – 0.3 (WW) |
| Whole blood (exposed persons) i       | ---                   | Up to 0.2 (WW) |
| Whole blood (smokers) i               | ---                   | ≤0.0002-0.006 (WW) |
| Whole blood (nonsmokers) i            | ---                   | <0.0002-0.002 (WW) |
| Urine (exposed persons) i             | ---                   | Up to 0.2 (WW) |
| Urine (unexposed persons) i           | ---                   | <0.0001-0.003 (WW) |

*Note the references below were sourced by Adriano (2001)

*Page et al. (1987); b Ainsworth and Rai (1987); c McLaughlin et al. (1996); d Lee and Keeney (1975); e µg/l; f Bowen (1979); g Holmgren et al. (1993); h Wolnik et al. (1983); i Stoeppler (1992); j Shacklette (1972); ** Dry Weight, *** Wet Weight
2.3.4 **Cadmium sorption onto soil**

Sorption is defined as “the action of soaking up (absorption) or attracting (adsorption) substances” in the Oxford dictionary of environment and conservation (Park 2007). The Oxford dictionary defined adsorption as “the process by which molecules of a gas, liquid or dissolved substance (in a condensed form) stick to the surface of a solid material, or less frequently on a liquid” while absorption is defined as “the penetration of one substance into or through another”. Also desorption is defined as “the release of atoms, molecules or ions that are attached to a solid surface” which is opposite of adsorption (Park 2007).

Adsorption/desorption processes are one of the main factors controlling metal concentration in soil (Tiller *et al.* 1984; Swift & McLaren 1991). After fertiliser application, Cd can accumulate in topsoil or subsoil via adsorption processes (Kim and Fergusson, 1992) and because of their chemical properties and high specific surface areas, soils have considerable capacity to bind heavy metals (Tanneberg & Jahn 2007). Trace metal adsorption to soil is controlled by the ion association and the ion exchange capacity of the soil (Sparks 2000). The adsorption process can occur when the surface-to-volume ratio (specific surface area) of the adsorbent is significantly high, which usually happens when the amount of clay-size mineral particles or organic matter molecules is considerable (Bleam 2012).

Sposito (1984) introduced two different groups of metal sorption in soils according to the affinity between adsorbent and adsorbate: inner-sphere and outer-sphere complexes. Where there is a covalent binding (no interposition) between the bathing solvent molecule, the surface functional group and the
bound molecule, then the complex formed is considered inner-sphere. If at least one molecule participates in the interposition, the complex would be outer-sphere. Electrostatic bonding mechanisms are included in outer-sphere surface complexes, and therefore outer-sphere surface complexes are less stable than inner-sphere surface complexes, which are included in ionic or covalent bonding (Sposito 1984). Cadmium adsorption in soil is mainly via inner-sphere complexation (Swift & McLaren 1991).

Rapid adsorption usually happens within a few seconds to hours (Sparks 2000). Ion association and binding can lead to fast adsorption while diffusion into micropores and interlayer spaces and the formation of surface precipitates occur during slow adsorption (Tanneberg & Jahn 2007). Tanneberg and Jahn (2007) showed for eight different soils that 59% of added Cd was adsorbed in the first 10 minutes of the adsorption process. Christensen (1984) also showed that 95% of Cd adsorption in loamy sand and sandy loam soils occurs in the first 10 minutes and equilibrium happened within the one hour, with no further adsorption increase for 67 weeks.

Loganathan et al. (2012) summarised Cd adsorption (inner-sphere) onto solid particles as occurring as one of four types: 1) nonspecific adsorption, 2) specific adsorption, 3) inorganic or organic ligand complexation and 4) precipitation or oc-precipitation (Figure 2.2).
Figure 2.2. Different kinds of Cd sorption mechanisms in soil (from Loganathan et al. 2012)

The assessment of the strength of Cd adsorption onto soil surfaces is important, because a low affinity of Cd with soil could lead to Cd leaching down through the soil profile, leading to groundwater pollution, whereas a high affinity of Cd for soil can lead to terrestrial pollution and accumulation (Christensen 1987).
2.3.5 Factors affecting cadmium adsorption onto soil

Different factors affect Cd adsorption onto soil including pH (García-Miragaya & Page 1978; Pardo 1997; Gray et al. 1999a), ionic strength (Boekhold et al. 1993), competing ions (Zasoski 1974; Christensen 1987; Naidu et al. 1994), ligand complexation (García-Miragaya & Page 1978; Boekhold et al. 1993), organic matter (Wilkens & Loch 1997; Gray et al. 1999a), the soil cation exchange capacity (CEC) (Haghiri 1974; He & Singh 1993; Gray et al. 1999a), Eh (redox potential), and Zn status (Adriano 2001).

2.3.5.1 pH

Metal adsorption to soil depends highly on the soil pH (Abd-Elfattah & Wada 1981; Gray et al. 1999a; Tanneberg & Jahn 2007) and with increasing soil pH, a sharp increase occurs in Cd adsorption until reaching maximum % adsorption (García-Miragaya & Page 1978; Naidu et al. 1994; Taylor & Theng 1995; Shaheen et al. 2015).

pH is recognized as the most important factor affecting the bioavailability of Cd (Kabata-Pendias & Pendias 2001; Kukier et al. 2004; Amini et al. 2005; Basta et al. 2005). Most metals are more soluble at low pH (< 6.0 for Cd) because carbonates, phosphates and other Cd-bearing solid phases dissolve at lower pH levels (Figure 2.3) (Adriano 2001).

Bolan et al. (2005) provided three reasons for increasing Cd availability as a result of pH decreasing: 1. A decrease in negative surface charge of soil occurs as a result of pH decrease, and therefore Cd adsorption would also decrease; 2. A decrease in hydroxyl species of metal cations (such as CdOH⁺) can occur due to a decrease in soil pH (Naidu et al. 1994);
3. Dissolution of Cd-bearing salts occurs under acidic conditions and therefore the Cd concentration increases in soil solution. The distribution of Cd complexes in soil also varies with soil pH (Hirsch & Banin 1990) (Figure 2.3).

![Diagram showing Cd species distribution in the solution of a typical calcareous soil](image)

Figure 2.3. Cd species distribution in the solution of a typical calcareous soil (from Hirsch & Banin 1990)

When the pH of soil is between 4 and 8, Cd adsorption increases rapidly and therefore this range of pH is called the “adsorption edge” (Loganathan et al. 2012), which shows when the soil is reaching the maximum potential of Cd adsorption and cannot adsorb more Cd. The adsorption edge of Cd in soil is lower than some other heavy metals such as Zn, Cu and cobalt (Co) (Spark et al. 1995; Loganathan et al. 2012). Tran et al. (1998) showed that for a sandy soil within the pH range of 5.5 to 6.5, for any 0.5 unit increase in pH, Cd adsorption doubled.
2.3.5.2 Ionic strength

An increase in ionic strength can decrease the solution activity of free metal ions and therefore reduce Cd adsorption (Boekhold et al. 1993; McLaughlin et al. 2000). The effect of ionic strength on adsorption also depends on soil surface properties (Naidu et al. 1994). Naidu et al. (1997) noted that an increase in ionic strength can decrease metal adsorption due to the influence on sorbate and sorbent properties. For example, on materials with permanent charge density, an ionic strength increase of NaClO₄, NaCl or Na₂SO₄ causes reduction in Cd adsorption (García-Miragaya & Page 1976; García-Miragaya & Page 1977; Kookana et al. 1999). Changes in ionic strength often cause soil pH variation and therefore Cd adsorption will change in response to both pH and ionic strength variation.

2.3.5.3 Competing ions, CEC and ligand complexation

A number of ions such as Ca²⁺ (calcium), Co²⁺, Cu²⁺ (copper), Pb²⁺, Ni²⁺ (nickel), Cr³⁺ (chromium), Al³⁺, Na⁺ (sodium) and Zn²⁺ (of which Zn is more significant, see section 2.3.8) compete with Cd in adsorption phenomena (Zasoski 1974; Christensen 1987; Homann & Zasoski 1987; Naidu et al. 1997; McLaughlin et al. 2000) and therefore may cause reductions in Cd adsorption onto soil (Tiller et al. 1979; Christensen 1987). For example, Zn on hydrous Mn oxides or unspecified clays (Zasoski 1974; Tiller et al. 1979), Pb on montmorillonite, illite and kaolinite (Bittell & Miller 1974), Pb, Cu and Zn on Fe oxyhydroxide and alumina oxide (Benjamin & Leckie 1980) can cause reductions in Cd adsorption to soil. According to the Irving-Williams series the stability of metals to form a complex shows this order:
Hg > Pb > Cu > Zn > Ni ≈ Co > Cd (Irving & Williams 1953), therefore all metals in the Irving-Williams series will compete with Cd for complex formation and reduce Cd adsorption onto soil. Christensen (1987) showed that mixtures of Ni, Co, and Zn and mixtures of Cr, Cu, and Pb, reduced Cd adsorption onto soil. Zinc was more effective than some other metals (such as Co and Ni) in competition with Cd, and this competition with Cd in adsorption processes was observed in both topsoil and subsoil samples (Christensen 1987).

Cation exchange capacity (CEC) is the interchange between a cation on the surface of a material and a cation in solution (Blakemore et al. 1987). Blakemore et al. (1987) defined soil CEC as “the amount of a cation that a soil can hold when a buffered or unbuffered salt solution is leached through the soil”. Positively charged metals such as Cd\(^{2+}\) can exchange with elements (e.g. Ca\(^{2+}\) and Na\(^{+}\)) associated with negatively charged surfaces in the soil (Cadmium Working Group 2008). Therefore, soils with a higher CEC show greater potential for Cd adsorption. CEC is an important factor in controlling the adsorption of Cd onto soils and an increase in CEC can enhance the pH buffering capacity of soils and consequently increase Cd adsorption (Adriano 2001). It is noteworthy that application of large quantities of phosphate can cause noticeable CEC increases (Bolan et al. 2003).

Cadmium complexation by inorganic ligands also affects Cd adsorption in soils. For example, chloride and cadmium can form CdCl\(^{+}\), which causes a reduction in Cd adsorption and consequently increases the availability of Cd to plants (McLaughlin et al. 1994; Zanders et al. 1996). In some studies, there was no clear impact of SO\(_4^{2-}\) on Cd adsorption (Benjamin & Leckie
1982; Homann & Zasoski 1987; Harmsen 1992), but others have reported Cd adsorption increases in the presence of SO$_4^{2-}$ (O'Connor et al. 1984).

2.3.5.4 **Organic matter**

Organic matter can increase the ion exchange capacity of soils and therefore metal ions would generally be less mobile in the presence of organic matter (Adriano 2001). Thus, Cd adsorption generally increases as soil organic matter content increases. Yuan and Lavkulich (1997) showed that 11% reduction in organic matters resulted in a 62% reduction in Cd adsorption. McBride et al. (1997) and Gray et al. (1999a) suggested that the influence of organic matter on Cd adsorption onto soil was important and Gray et al. (1999a) concluded that organic matter alone can explain 24% of variation of Cd adsorption for different soils.

2.3.5.5 **Soil composition**

Soil texture can affect the adsorption behavior of Cd onto soils. For example, Holmgren et al. (1993) showed that generally the Cd concentration of soil increases with increasing clay content. Singh and Myhr (1997) showed in a field in Norway, that Cd did not leach significantly within the soil due to the large clay content and significant adsorption onto topsoil. However, Shuang et al. (2009) reported that soils with the highest clay content had the lowest amount of Cd adsorption, when the clay minerals had greater amounts of hydrous mica and kaolinite.

These soil properties are interrelated, and the highest amount of one effective factor cannot solely control metal adsorption because of the effects
of other controlling soil properties (Roberts 1981); for example, pH may strongly correlate with clay minerals, oxides, or organic matter, and therefore camouflages their effect on Cd and metal adsorption (Holm et al. 2003). Holm et al. (2003) showed that under the conditions of constant pH, gibbsite was the only mineral that may effect the distribution of Cd in soil. Kim and Fergusson (1992) removed organic matter, iron and manganese oxides in some soil samples and then compared the adsorption behaviour of different soil samples. Results showed that Cd adsorption to soil decreased according to this order: clay (< 3.9 µm) > whole soil > soil without iron and manganese oxides > silt (3.9 – 63 µm) > sand (63 – 563 µm) > soil without organic matter > silica sand. Therefore the clay fraction was the most efficient factor in Cd adsorption (García-Miragaya & Page 1976; Wold & Pickering 1981; García-Miragaya et al. 1986).

Considerable variation in the concentration of Cd has been observed in the Waikato region of New Zealand (Zanders 1998). The hierarchy of Cd concentration related to soil types was in this order: brown granular loam (Granular Soil) > gley recent soils (Gley Soil) > integrated between yellow brown earths and yellow brown sands (Brown Soil) > yellow brown earths (Brown/Ultic Soil) > steepland soils related to yellow brown earths (Brown/Ultic Soil) > yellow brown loam (Allophanic Soil) > yellow brown sands (Brown/Ultic Soil). However, an analysis of variance showed that only 9% of the Cd concentration variability in topsoil could be explained by parent materials in soils (Zanders 1998). Zanders argued that Cd concentration variability was mainly related to the fertiliser application history rather than soil type.
The principal differences in mineralogy between soils relate to the various clay minerals present (Ashman & Puri 2002). Differences in clay structure (i.e. Al:Si ratios of 1:1 and 2:1 clays) cause different charge characteristics—most importantly the charge of 2:1 clays which can be both permanent and variable, but the charge of 1:1 clays is always variable (Ashman & Puri 2002). For example, allophane and halloysite are two different types of clay minerals and allophane has mainly variable charges with a very large specific surface area with a high anion (low pH) and cation (high pH) adsorption capacity, whereas halloysite contains both permanent and variable charge sites. The different proportion of halloysite and allophane in soils has the potential to modulate the surface charge of the soils depending on pH (Sollins et al. 1988).

In permanent charge clays, isomorphous substitution of lower and higher valence ions leads to alteration of the crystal lattice structure and therefore the electric charge on clay particles. In the variable charge clays (such as allophane), the protonation and deprotonation of edge hydroxyl groups controls surface charge (Sollins et al. 1988). Therefore, because of the different range of allophane structures depending on Al:Si ratios, any generalization about the adsorption of heavy metals on allophane would not be comprehensive (Itami & Yanai 2006).

Tanneberg and Jahn (2007) showed that by increasing the allophane content of soil, a sharp decrease in Cd adsorption occurred when pH decreased from 7 to 4, and concluded that Cd adsorption/desorption was more dependent on soil pH rather than allophane content.
Yuan et al. (2002) showed that although allophane was not very efficient for Cd adsorption, the adsorption capacity of allophane could be enhanced by adding organic matter; however, much of the Cd adsorbed to allophanic soils can be desorbed easily (the ratio of desorbed Cd to adsorbed Cd in allophanic soils was 94% at pH 5.0 and 93% at pH 5.5). Generally, soils with low negative surface charge or sandy nature have also low adsorption capacities and therefore include considerable Cd mobility (Boekhold & Van der Zee 1991; Kookana et al. 1994).

In regard to the all aforementioned factors affecting Cd adsorption to soil, King (1988) reported that 96% of variation in Cd adsorption depended on pH, organic matter and ammonium oxalate-extractable Fe for 13 topsoil samples. Christensen (1989) also showed that pH and CEC were the most important factors controlling the Cd adsorption for 63 soils from Denmark. Statistical analysis showed that the clay content and clay minerals composition were not significant factors controlling the Cd distribution between the soil sample and solution. Reiser et al. (2014) also showed that soil pH, Fe and total Cd concentrations were the most important factors affecting Cd bioavailability in soil samples from 69 pastures in New Zealand.

In general it is considered that pH was the most important factor controlling Cd sorption followed by CEC and organic matter content (Table 2.2). Therefore changes in soil pH can probably mask the importance of some other important factors for the amount of Cd adsorption (Christensen 1989).
Table 2.2. Different factors affecting Cd adsorption to soil (from Loganathan et al. 2008)*

<table>
<thead>
<tr>
<th>Factor</th>
<th>Cd sorption decrease/increase</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Increase as pH increase</td>
<td>Williams and David (1973); Merry (1988); Boekhold and Van der zee (1992); McBride et al. (1997); Gray et al. (1998)</td>
</tr>
<tr>
<td>Fe, Al, Mn oxides and allophane</td>
<td>Increase as these colloids increase</td>
<td>McLaughlin et al. (1996); Zasoski and Burau (1988)</td>
</tr>
<tr>
<td>Layer silicates</td>
<td>Increase due to existence of silicate layer</td>
<td>McLaughlin et al. (1996)</td>
</tr>
<tr>
<td>Organic matter</td>
<td>Increase with increase in organic matter</td>
<td>Boekhold and Van der zee (1992); McBride et al. (1997); Gray et al. (1998); Gray et al. (1999b); Gray et al. (1999a)</td>
</tr>
<tr>
<td>Ions in solution</td>
<td>Decrease as Cl and Zn concentration increase</td>
<td>Manoharan et al. (1996); McLaughlin et al. (1996); Bolan et al. (1999); Adriano (2001)</td>
</tr>
<tr>
<td>Eh (redox potential)</td>
<td>Increase with redox potential increases (CdS formation) and decrease with Fe/Mn oxide dissolution</td>
<td>Adriano (2001)</td>
</tr>
<tr>
<td>CEC</td>
<td>Increase as CEC increases</td>
<td>Bolan et al. (2005)</td>
</tr>
</tbody>
</table>

*Note the references in the table were sourced by Loganathan et al. (2008)

2.3.6 Cadmium accumulation in topsoil

The majority of Cd applied in P fertilisers is retained in the topsoil or the root zone of soil due to the higher organic matter of surface soil (Loganathan et al. 1995; Roberts et al. 1996; Loganathan & Hedley 1997; Zanders et al. 1999). Loganathan and Hedley (1997) showed that about 90% of Cd from phosphate fertiliser applied to a NZ pasture over 10 years had accumulated in the top 12 cm of soil.
The residence time of Cd in soil is of concern because Cd can remain in the food chain for years and be taken up by plants, animals and humans. The residence time of Cd was shown to be between 200 to 700 years in crop soils (Loganathan & Hedley 1997). For fertilisers with low amounts of Cd (1 to 20 mg Cd kg⁻¹ P₂O₅) the accumulation of Cd is slow or the concentration decreases after 100 years of fertiliser application, while for fertilisers with Cd concentration > 60 mg Cd kg⁻¹ P₂O₅, the accumulation of Cd is high even 100 years after fertiliser application (CSTEE 2002). According to a NZ fertiliser industry report, to prevent the accumulation of Cd in NZ soils, there should be a ~80% reduction in the current standard of 280 mg Cd kg P⁻¹ (i.e. 50 mg Cd kg P⁻¹) in phosphate fertilisers (Ballance Agri-Nutrients 2005). The process of Cd accumulation in pastoral and horticultural soils leads to a loss in soil resource capacity (Figure 2.4) (Kim 2005).
2.3.7 Cadmium leaching and redistribution throughout the soil profile

Cadmium leaching from soil depends on soil properties (sections 2.3.5.1 to 2.3.5.6, soil pH, ionic strength, competing ions, CEC, organic matter and soil texture). Soil macro-pores can support bypass flow of water and Cd movement down through the soil (Dowdy et al. 1991).

McLaren et al. (2004) studied the leaching of Cd from five contrasting soils including three soils (Waikuku loamy sand, Lismore stony silt loam and Eyre

Figure 2.4. The schematic pattern of contaminant (here Cd) accumulation in soils which cause reduction in soil resource capacity (from Kim 2005)
shallow silt loam) under forest and two soils (Templeton fine sandy loam and Horotiu sandy loam) under pasture. Following a single application of sewage sludge, the leachate of metals was assessed for a period of three years. The application of sewage sludge caused a decrease in soil pH and an increase of Cd, Ni and Zn leachate. Soil type (soil properties) and land use (pasture or forest) were considered to be the important factors controlling metal mobility in soil. McLaren et al. (2004) stated that Horotiu soils have high organic matter, iron and allophanic minerals and therefore a higher tendency to absorb metals, and generally these properties are responsible for the lower amount of metal leaching from Horotiu soil. However, the total water drainage from the Horotiu soil was much higher than the other soil types investigated. The results showed that small proportions (less than 1%) of applied metals were leached even after three years of sewage sludge application.

The potential mobility of Cd in soils was shown to be controlled by adsorption and desorption on colloid surfaces (Gray et al. 2003a). Cadmium leaching from sandy soils receiving high inputs of Cd (more than 50 g ha⁻¹yr⁻¹) may exceed the maximum permitted amount of Cd in groundwater (Kookana et al. 1999). For example, Lund et al. (1976) reported that Cd moved to a depth of up to 3 m in a coarse-textured soil under sludge drying ponds for more than 20 years. Cadmium moved down 90 cm in a sandy soil at a wastewater application field after 29 year of wastewater application (Streck & Richter 1997).

Generally, there is no consensus on the potential for Cd mobility in soils (Gray et al. 2003a) and although some research has shown that Cd was not significantly mobile in the soil profile (Singh & Myhr 1997; Martin & Kaplan
1998), a number of other studies reported that Cd can significantly translocate throughout the soil profile (Williams & David 1976; Rothbaum et al. 1986).

2.3.8 Relationship between Cd and Zn

Zinc and Cd have many common properties (Lagerwerff 1972). Cadmium is usually associated with Zn in the Earth’s crust (Viinogradov 1959), however, the natural amount of Cd in soil is much less than Zn. In some regions of NZ, Zn is used in pastoral agriculture to relieve facial eczema in cattle and sheep (Kim 2005). In addition, there are a number of compounds containing Zn, such as antibiotics, antidotes, antifungals, anti-inflammatoryatories, antimicrobials, oral nutrient/electrolytes, parenteral nutrient/electrolytes, probiotics and skin/coat conditioners used on pastoral farms (Kim 2005). Because of the ability of Zn containing products to contain Cd, agrochemicals which contain Zn may also be a source of Cd (Gaw et al. 2006). Gaw et al. (2006) showed a strong correlation between Zn and Cd in horticultural samples, which suggested a common source for Cd and Zn, and some research showed that fertiliser applications led to elevated concentrations of Zn in NZ soils (Taylor & Percival 2001). Because of the similar properties of Cd and Zn, Hooda (2010) suggested that it was important to consider both metals to assess the behaviour of each in soil.

Zinc can compete with Cd in adsorption processes and decrease plant uptake of Cd (Chaney 1973; Mengel & Kirkby 2004). Homma and Hirata (1984) showed that when the concentration of Cd and Zn ions was lower than 1.0 µmol L⁻¹, the uptake of Zn and Cd by rice was the same. Whereas, at higher concentrations,
the amount of Zn ions taken up by rice was more than twice the uptake of Cd ions.

To assess the effects of fertiliser application on the amount of Cd in soils, with a known amount of natural Cd and Zn or a known Zn/Cd ratio in unfertilised soil, the comparison between Zn/Cd ratio at different depths in fertilised and unfertilised soils can be used to distinguish whether the sources of Cd have natural origins, or anthropogenic ones. This is a helpful approach that may help in determining how far Cd transfers through the soil profile. Loganathan et al. (1995) reported that the Zn/Cd ratio increased within the soil profile of agricultural land and showed a decrease in Cd concentration through soil profile and also confirmed that phosphate fertiliser application increased the accumulation of Cd in topsoils. Also, the results of Zanders et al. (1999) on agricultural and non-agricultural soils of the Waikato region confirmed that the Zn/Cd ratio in fertilised soils was between 2.5 to 10 times lower than soils from native bush. The Zn/Cd ratio in NZ native soils is generally greater than in pastoral soils (Table 2.3).

Table 2.3. The mean Zn/Cd ratio in native and pastoral soils of New Zealand (from Roberts et al. 1994) (the soil classification in this table has been superseded and is not used anymore)

<table>
<thead>
<tr>
<th>Soil group</th>
<th>Alluvial$^a$</th>
<th>Brown granular loams (Brown Soil)</th>
<th>Gley Peat Yellow brown earths (Brown/Ultic Soil)</th>
<th>Peat Yellow brown loams (Allophanic Soil)</th>
<th>Yellow brown pumice soils (Pumice Soil)</th>
<th>Yellow-grey earths (Pallic Soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>765</td>
<td>387</td>
<td>760</td>
<td>333</td>
<td>754</td>
<td>475</td>
</tr>
<tr>
<td>Pastoral</td>
<td>633</td>
<td>239</td>
<td>268</td>
<td>66</td>
<td>390</td>
<td>179</td>
</tr>
</tbody>
</table>

$^a$ Not a defined soil group in the New Zealand Genetic Soil Classification
2.4 Cadmium in New Zealand soils

New Zealand soils are young and have high organic matter in comparison to many other countries (McLaughlin et al. 2000; Cadmium Working Group 2008). Most NZ soils are acidic with topsoil pH ranges from 4.5 to more than 6.0, and for peat soils, pH may vary from 3.5 to 3.8 (During 1972). Furthermore, the NZ climate is highly variable (New Zealand Institute of Chemistry 2016), which has a high bearing on soil properties geographically.

New Zealand witnessed the greatest growth in phosphate fertiliser use for the OECD countries from 76,000 t in 1990 to 174,000 t in 2002 (OECD 2008). Fertiliser application directly supports a significant proportion of NZ agricultural production, and without fertiliser use, NZ soils would be suitable to support only 25 to 50% of the current number of grazing animals or crops (Statistics New Zealand 2006). Due to concern about Cd accumulation in soil, some EU and non-EU member states including New Zealand have set restrictions on the concentration of Cd in superphosphate fertilisers (Table 2.4).

Table 2.4. Legal, recommended or voluntary amount of Cd in superphosphate in a number of countries (Mortvedt 1995; Furness 1998; European Commission 2016)

<table>
<thead>
<tr>
<th>Country</th>
<th>Cd (mg kg\textsuperscript{-1} P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>343</td>
</tr>
<tr>
<td>Australia</td>
<td>300</td>
</tr>
<tr>
<td>New Zealand</td>
<td>280</td>
</tr>
<tr>
<td>Belgium</td>
<td>200</td>
</tr>
<tr>
<td>Austria</td>
<td>170</td>
</tr>
<tr>
<td>Germany</td>
<td>140</td>
</tr>
<tr>
<td>Denmark</td>
<td>110</td>
</tr>
<tr>
<td>Sweden</td>
<td>100</td>
</tr>
<tr>
<td>Norway</td>
<td>100</td>
</tr>
<tr>
<td>Switzerland</td>
<td>50</td>
</tr>
<tr>
<td>Finland</td>
<td>50</td>
</tr>
<tr>
<td>Netherlands</td>
<td>40</td>
</tr>
</tbody>
</table>
The recommended level of Cd in superphosphate in most of the EU member states is lower than in New Zealand (Table 2.4).

In New Zealand, the main sources of Cd are phosphate fertilisers used in agriculture (Gray et al. 1999b; Loganathan et al. 2003; Schipper et al. 2011) with lower impacts from atmospheric or industrial activities (Loganathan et al. 2003). The major type of farming in New Zealand is grazed pasture, which covers 13.8 million hectares (Loganathan et al. 2003).

The accumulation rate of Cd in NZ agricultural soil differs from region to region because of the history of phosphate fertiliser use, land use, soil type, weather and climate, sampling depth, and soil dry bulk density (Cadmium Working Group 2008).

Taylor et al. (2007) showed that the average concentration of Cd in soil in NZ pastures was 0.43 mg kg$^{-1}$ (range 0-0.77 mg kg$^{-1}$), which was more than twice the NZ background concentration of 0.16 mg kg$^{-1}$. The mean concentration of Cd in topsoils of all agricultural lands was 0.35 mg kg$^{-1}$ (range 0-2.52 mg kg$^{-1}$) (Taylor et al. 2007; Cadmium Working Group 2011a). In a more recent study of Cd concentration in NZ pasture soils, the Cd concentration in soil had increased and ranged between 0.25 and 1.58 mg kg$^{-1}$ (mean of 0.89 mg kg$^{-1}$). A high proportion of samples from farmland under intensive dairy farming was considered to be the most probable reason for the large discrepancy (Reiser et al. 2014).

Land use affects Cd accumulation, e.g. Taylor et al., (2007) showed that dairy lands had the highest concentration of Cd (mean of 0.73 mg kg$^{-1}$), followed by kiwifruit (0.71 mg kg$^{-1}$), berries (0.68 mg kg$^{-1}$), orchards (0.66 mg kg$^{-1}$), market gardens (0.46 mg kg$^{-1}$), drystock pasture (0.40 mg kg$^{-1}$) and cropping soils
Taylor’s regional assessment of Cd showed that the highest concentrations of Cd in New Zealand were in Taranaki (mean of 0.69 mg kg\(^{-1}\)) followed by the Waikato (mean of 0.55 mg kg\(^{-1}\)) and Bay of Plenty (mean of 0.53 mg kg\(^{-1}\)), because of the long history of dairy and horticulture and also the soil types (for example, soils driving from volcanic ash require more P fertilisers) (Taylor et al. 2007).

A recent report on Cd in NZ soil showed that the mean concentration of Cd in soil ranged from < 0.01 to 2.14 mg kg\(^{-1}\) (mean 0.44 mg kg\(^{-1}\)) (Stafford et al. 2014). In agreement with Taylor et al. (2007), the highest concentration of Cd occurred under dairy (mean of 0.59 mg kg\(^{-1}\)) and orchard lands (mean of 0.55 mg kg\(^{-1}\)). Waikato (mean of 0.74 mg kg\(^{-1}\)), Bay of Plenty (mean of 0.70 mg kg\(^{-1}\)) and Taranaki (mean of 0.58 mg kg\(^{-1}\)) showed the highest concentrations of Cd, and in comparison to the results of Taylor et al. (2007), the concentration of Cd in the Waikato and Bay of Plenty regions exceeded the amount of Cd in Taranaki (Stafford et al. 2014).

Different values have been reported for the natural background concentration of Cd in NZ soils: 0.2 mg kg\(^{-1}\) (Roberts et al. 1994), 0.1 mg kg\(^{-1}\) (Anon 2007) and 0.16 mg kg\(^{-1}\) (Taylor et al. 2007). The national average accumulation of Cd during 2005-2010 decreased (approximately 5 µg Cd kg\(^{-1}\) soil yr\(^{-1}\)), probably because of the reduction of Cd in fertilisers since 1997 (Cadmium Working Group 2011a). New Zealand phosphate fertilisers ultimately derived from Nauru and Christmas Island phosphate rocks, and applied to NZ agricultural soils from the late 1800s up to 1996 (Syers et al. 1986). On average, the amount of Cd in Nauru rock phosphate is about 450 mg Cd kg\(^{-1}\) P (Cadmium Working Group 2008), or 34-69
mg Cd kg\(^{-1}\) in fertilisers derived from Nauru and Christmas Island rocks (Rothbaum et al. 1986). Since 1997, the main source of phosphate fertilisers has changed from Nauru to a variety of other sources with lower amounts of Cd, and the fertiliser industry has decided to produce fertilisers with no more than 280 mg Cd kg\(^{-1}\) P (26 mg Cd kg\(^{-1}\) superphosphate fertiliser) (Table 2.5) (Cadmium Working Group 2008; Cadmium Working Group 2011b).

Table 2.5. The concentration of phosphate (mg kg\(^{-1}\)) and industry limit on Cd (mg kg\(^{-1}\)) in NZ phosphate fertilisers (from Kim 2005)

<table>
<thead>
<tr>
<th>Element</th>
<th>Single/double superphosphate</th>
<th>Triple superphosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate concentration as %P(_2)O(_5)</td>
<td>18–21</td>
<td>45</td>
</tr>
<tr>
<td>Phosphate concentration as %P</td>
<td>8.73</td>
<td>19.6</td>
</tr>
<tr>
<td>Industry limit of Cd as mg Cd kg(^{-1}) P</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>Industry limit of Cd as mg Cd kg(^{-1}) P(_2)O(_5)</td>
<td>122</td>
<td>122</td>
</tr>
<tr>
<td>Industry limit of Cd as mg Cd kg(^{-1}) fertiliser</td>
<td>24.4</td>
<td>55.0</td>
</tr>
</tbody>
</table>

A threshold value of 1.8 mg kg\(^{-1}\) has been identified for Cd in NZ soils (MAF, 2011) and while the concentration of Cd is often lower than the threshold value in NZ soils, some studies have shown higher concentrations in NZ agricultural soils (Table 2.6).
Table 2.6. Average total concentration of Cd (mg kg\(^{-1}\)) in some NZ surface soils (the amount and length of phosphate fertiliser application are different)

<table>
<thead>
<tr>
<th>Soil sample depth (cm)</th>
<th>Extraction method</th>
<th>Agricultural soils</th>
<th>Number of samples</th>
<th>Non-fertilised soils</th>
<th>Number of samples</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-7.5</td>
<td>HClO(_4)-HNO(_3)</td>
<td>0.44 (0.04-1.53)</td>
<td>312</td>
<td>0.20 (0.02-0.77)</td>
<td>86</td>
<td>(Roberts \textit{et al.} 1994)</td>
</tr>
<tr>
<td>0-15</td>
<td>4M HNO(_3)</td>
<td>0.69 (0.46-1.91)</td>
<td>22</td>
<td>----</td>
<td>----</td>
<td>(Taylor &amp; Percival 1992)</td>
</tr>
<tr>
<td>0-10</td>
<td>HCl-HNO(_3) (Aqua Regia)</td>
<td>0.89 (0.25-1.58)</td>
<td>69</td>
<td>----</td>
<td>----</td>
<td>(Reiser \textit{et al.} 2014)</td>
</tr>
<tr>
<td>0-10</td>
<td>Aqua Regia</td>
<td>0.71 (0.10-2.0)</td>
<td>215</td>
<td>0.11 (0.03-0.30)</td>
<td>36</td>
<td>(Taylor &amp; Kim 2009)</td>
</tr>
<tr>
<td>0-3.0</td>
<td>Aqua Regia</td>
<td>0.32</td>
<td>----</td>
<td>0.18</td>
<td>----</td>
<td>(Loganathan \textit{et al.} 1996)</td>
</tr>
<tr>
<td>3.0-7.5</td>
<td>Aqua Regia</td>
<td>0.24</td>
<td>----</td>
<td>0.15</td>
<td>----</td>
<td>(Loganathan \textit{et al.} 1996)</td>
</tr>
<tr>
<td>0-7.5</td>
<td>HNO(_3)</td>
<td>0.27</td>
<td>----</td>
<td>0.06</td>
<td>----</td>
<td>(McDowell 2010)</td>
</tr>
<tr>
<td>0-15</td>
<td>4M HNO(_3)</td>
<td>0.85</td>
<td>58</td>
<td>----</td>
<td>----</td>
<td>(Taylor 1997)</td>
</tr>
<tr>
<td>0-3.5</td>
<td>HNO(_3)-HF</td>
<td>0.64</td>
<td>10</td>
<td>0.18</td>
<td>10</td>
<td>(Zanders \textit{et al.} 1999)</td>
</tr>
<tr>
<td>0-7.5</td>
<td>HNO(_3)</td>
<td>0.53 (0.03-1.34)</td>
<td>29</td>
<td>----</td>
<td>----</td>
<td>(Gray \textit{et al.} 1999a)</td>
</tr>
</tbody>
</table>

McLaughlin \textit{et al.} (1996) investigated five different fertiliser contaminants including As (arsenic), Cd, Hg, Pb and F (fluorine) and concluded that Cd and F were among the pollutants with the highest risk to the NZ environment because of the less time taken to double their concentration in topsoil (<100 yr) in comparison to the other pollutants (>1000 yr). Loganathan \textit{et al.} (2008) estimated that it took about 36 years to double the concentration of Cd in NZ pastures at the current annual rate of application of 30 kg P ha\(^{-1}\) yr\(^{-1}\) (Table 2.7), and therefore the assessment of Cd accumulation and its risk in NZ agricultural soils are of upmost importance.
Table 2.7. Estimated time of doubling Cd concentration in topsoil (0-10 cm) of NZ grazed pastures in condition of annual application of P fertiliser (from Loganathan et al. 2008)

<table>
<thead>
<tr>
<th>Input (g ha⁻¹)</th>
<th>Pasture uptake (g ha⁻¹)</th>
<th>Animal intake (g ha⁻¹)</th>
<th>Animal removal (g ha⁻¹)</th>
<th>Net rate of addition (g ha⁻¹ yr⁻¹)</th>
<th>Background soil concentration (mg kg⁻¹)</th>
<th>Years to double Cd concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd 8.4</td>
<td>2.0</td>
<td>1.6</td>
<td>0.0016</td>
<td>8.3984</td>
<td>0.3</td>
<td>36</td>
</tr>
</tbody>
</table>

*a 30 kg P ha⁻¹ yr⁻¹ (limit of 280 mg Cd kg⁻¹ P)
*b 10,000 kg dry matter ha⁻¹ yr⁻¹, 0.2 mg Cd kg⁻¹ dry matter
*c 80% utilization of pasture by animals
*d 0.1% Cd permanent removal
*e Column 2 minus column 5
*f Bulk density of 1 g cm⁻³

The New Zealand Fertiliser Manufacturers’ Research Association (NZFMRA) introduced a model called CadBal to manage and predict the future concentration of Cd in NZ soils (Roberts & Longhurst 2005). Using CadBal and a national data set of Cd in 1794 topsoils collected from 1989 to 1995 and 2000 to 2007, Cd had been showed to accumulate more in Brown Grey Clay Loams, Yellow Brown Loam and Yellow Brown Podzol Soils than Alluvial, Yellow Brown Earths and Yellow Grey Earth and Gley Soils (Cadmium Working Group, 2008). These differences were attributed to differences in input data used in the CadBal model such as soil dry bulk density and leaching losses. However, Zanders (1998) showed that only 9% of the Cd concentration variability in topsoil can be explained by the soil type and the variability in Cd concentration is mainly related to the fertiliser application. CadBal has been designed based on New Zealand Soil Genetic Classification, which has been superseded, and needs to be translated to the current New Zealand soil classification system introduced by Hewitt (1998).
2.4.1 Cadmium studies at the Winchmore long-term fertiliser and irrigation trial

There have been few long-term studies of the fate of Cd in NZ soils with the major exception of the Winchmore irrigation and fertiliser trials. The Winchmore research farm is located in Canterbury, New Zealand (171° 48' E, 43° 47' S, altitude of 160 m and annual rainfall of 740 mm) and was established in the late 1940s (Rickard & Moss 2012). The soil at Winchmore is Lismore Stony Silt Loam (Orthic Brown [New Zealand], Udic Ustochrept [USDA]) which is from moderately weathered greywacke loess (Condron et al. 2006). Two long-term trials were installed at this farm including a long-term fertiliser trial (since 1952) and a long-term irrigation trial (since 1949). McDowell (2012) investigated the Cd accumulation rate in the long-term grazed pastures of Winchmore for three fertiliser application rates (no fertiliser applied, 188 kg (18 kg P ha⁻¹) and 376 kg (36 kg P ha⁻¹) superphosphate applied annually) as well as two irrigation rates (dryland treatment and irrigation applied when the topsoil gravimetric moisture level reached 20% moisture with annual application of 250 kg superphosphate). Cd concentrations were determined at three soil depths: 0-7.5, 7.5-15 and 15-30 cm and the results showed that the fertilised soils were significantly enriched with Cd in comparison to native soils, and that topsoil (0-7.5 cm) was more concentrated than the two other depths (McDowell 2012). McDowell (2012) showed that the trend of Cd accumulation started to plateau around 1997.

The concentration of Cd in topsoil (0-7.5 cm) of dryland soil was higher than irrigated soil, however, the concentration of Cd at depths of 7.5-15 and 15-30 cm in dryland soils was lower than in irrigated soils, implying the downward
movement of Cd through the soil (Figure 2.5). The Winchmore site was border
dyke irrigated and therefore outwash and draining into irrigation bays and other
waterways may occur (McDowell 2010).

Figure 2.5. Mean concentration of Cd in the Winchmore long-term fertiliser
and irrigation trials (from McDowell 2012) (SSP, single superphosphate)
Overall there was good evidence that irrigation enhanced Cd loss due to translocation down the profile (Figure 2.5) coupled with increased plant and subsequent animal uptake at Winchmore (McDowell 2012).

### 2.4.2 Cadmium status of the Waikato region

The Waikato region is about 2.5 Mha with only about 1% urban land. Pastoral agriculture covers 52% of the region, including mainly dairy, beef and sheep farming (Taylor et al. 2010; Waikato Regional Council 2011). Waikato region soils are mostly acidic (Kim 2005) and therefore the bio-availability of applied Cd to the soils would be expected to be significant. From 1939 to 2002, the average net Cd accumulation rate was 9.0 µg kg\(^{-1}\) yr\(^{-1}\) and the maximum net Cd accumulation rate was 18.3 µg kg\(^{-1}\) yr\(^{-1}\) in topsoils (0-10 cm) under pastures in the Waikato (Kim 2005). About 8.3 tons of Cd is being applied to Waikato soils annually due to phosphate fertiliser application. In 2005, the concentration of Cd in 14% of pastoral soils in the Waikato region exceeded the recommended amount of 1 mg kg\(^{-1}\) and all of the pastoral soils with Cd concentrations above 1 mg kg\(^{-1}\) were dairy farms which had received larger amounts of superphosphate fertilisers (Kim 2005).

In 2010, the Cd concentration in about 12% of dairy, 16% of drystock, 25% of horticultural and 1% of urban soils sampled in the Waikato region exceeded the suggested recommended value (1 mg kg\(^{-1}\) Cd) (Taylor et al. 2010). Research completed in 2014 showed that the Waikato region had the highest burden of Cd in soils out of the different regions of New Zealand (Stafford et al. 2014).
2.4.3  Current management plan for New Zealand soil cadmium

The Cadmium Working Group (2011a) introduced a tiered system to manage Cd concentration in NZ soils:

- Tier 0: Cd concentration < 0.6 mg kg\(^{-1}\), no limitation on the phosphate fertiliser application is considered, however, a five-yearly screening soil test is required to check the status of Cd
- Tier 1: 0.6 ≤ Cd concentration < 1.0 mg kg\(^{-1}\), restriction on the products and application rates to minimise the accumulation of Cd, and also using approved programmes to test the concentration of Cd every five years
- Tier 2: 1 ≤ Cd concentration < 1.4 mg kg\(^{-1}\), a Cd balance program is required to manage the application rates of Cd to ensure that the concentration of Cd does not exceed the acceptable threshold in the next 100 years
- Tier 3: 1.4 ≤ Cd concentration < 1.8 mg kg\(^{-1}\), a Cd balance program and further management are required to manage the application rates of Cd to ensure that the concentration of Cd does not exceed the acceptable threshold in the next 100 years
- Tier 4: Cd concentration ≥ 1.8 mg kg\(^{-1}\), no further application of Cd (Cadmium Working Group 2011a; 2011b; 2012)

The threshold values do not reflect the maximum recommended amount of Cd for soil and therefore do not imply that soil can be contaminated up to the level of the threshold value (Kim 2005). The Cadmium Working Group (2011a) suggested that: “The thresholds at which tiers are implemented will correspond to the guideline values for Cd management in New Zealand” and “Where the
sampling is conducted on land management units, the highest soil Cd result should be adopted or further investigation carried out.”

Farm management actions for farms with Cd concentrations of more than the threshold value (1.8 mg kg\(^{-1}\)) would be the application of fertilisers with very low Cd contents, withholding of phosphate fertilisers altogether, dilute the Cd of surface soil by ploughing the soil to a depth of at least 30 cm or changing the land use to decrease the uptake of Cd (Sneath 2015).

Changes in land use need to be managed because, for example, the guideline values of Cd in residential soils are less than pastoral soils. Therefore, before changing the land use, the amount of Cd in the land should be assessed. Table 2.8 shows the soil guideline values according to the land use and therefore the required control (Kim 2005).

<table>
<thead>
<tr>
<th>Control need</th>
<th>Residential soil</th>
<th>Pastoral soil</th>
<th>Horticultural soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human and ecological health protection (home produce consumption)</td>
<td>1.0 (pH 6)(^a)</td>
<td>1.4(^b)</td>
<td>1.4(^b)</td>
</tr>
<tr>
<td>Future land use protection</td>
<td>1.0 (pH 6)(^a)</td>
<td>1.0 (pH 6)(^a)</td>
<td>1.0 (pH 6)(^a)</td>
</tr>
<tr>
<td>Based on the trading partners requirements</td>
<td>none</td>
<td>1.0(^c)</td>
<td>1.0(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Note the references below were sourced by Kim (2005)  
\(^a\) UK Environment Agency (2002a); \(^b\) CCME (2003); \(^c\) NZWWA (2003)

2.5 Cadmium uptake by plants

Cadmium can be absorbed into plant tissues, and therefore subsequently ingested by animals and humans that consume the plants (Van der Voet et al. 1994; Mahar et al. 2015). The concentration of Cd in plants is usually highly correlated with
the total concentration of Cd and P in soil (Reiser et al. 2014). The mobile species of Cd that can be taken up by plants is in the form of divalent ion \((\text{Cd}^{2+_{\text{aq}}})\) (Kim 2005) and the most important factors affecting Cd uptake by plants are the crop species and cultivar, plant tissue types, the age of leaf, metal interaction, form of added Cd to soil such as fertiliser or atmospheric deposition, soil properties, and the plants ability to adsorb Cd (Homburg & Brummer 1990; He & Singh 1993; Cadmium Working Group 2008; Pérez & Anderson 2009). Cadmium accumulation is in the order of leafy vegetables > root vegetables > grain crops > fruit (Cadmium Working Group 2008). Overall, the concentration of Cd in different parts of a plant is as follows: roots >> stalk base >> shoots (stems/sheaths > leaves) > grain (or fruit) (Adriano 2001). The major pathway for Cd uptake by plants is root adsorption (Zanders 1998). To manage Cd uptake, consideration needs to be given when switching from one land use to another (such as changing from dairy farms to a number of horticultural crops or leafy vegetables which are more sensitive to the Cd level) (Cadmium Working Group 2008). Lime application to agricultural soils is the common way to decrease Cd uptake by plants and has been recommended in many studies (Louekari 1996; McLaughlin et al. 1996; Loganathan et al. 2003). However, lime application can be limited by financial and practical limitations and the tolerable level of alkalinity for plants (Kim 2005). Therefore decreasing the amount of Cd uptake due to the application of lime is not always the best solution. The NZ Ministry for the Environment (MfE) introduced equation 2.1, to describe the relationship between Cd concentration in soil and plant uptake. Equation 2.1 is based on the results of 168 data points from 21 studies including 102 data points for green vegetables and 66 for root and tuber vegetables (MfE 2011) (Table 2.9).
\[
Ln (\text{plant uptake}) = a + b \times \ln (\text{soil Cd}) + c \times \text{soil pH}
\]  
\hspace{1cm} (2.1)

(MfE 2011)

Table 2.9. Coefficients and variability percentage (%Var) for Equation (2.1) (from MfE 2011)

<table>
<thead>
<tr>
<th>Vegetable type</th>
<th>ln (plant Cd)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>%Var</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data (n=168)</td>
<td>4.98</td>
<td>0.728</td>
<td>-0.764</td>
<td>58.0</td>
<td></td>
</tr>
<tr>
<td>Green (n=102)</td>
<td>4.58</td>
<td>0.759</td>
<td>-0.626</td>
<td>68.1</td>
<td></td>
</tr>
<tr>
<td>Root/tuber (n=66)</td>
<td>4.73</td>
<td>0.600</td>
<td>-0.838</td>
<td>58.6</td>
<td></td>
</tr>
</tbody>
</table>

The UK Environment Agency Department for Environmental, Food and Rural Affairs (DEFRA) also introduced two equations (equations 2.2 and 2.3) for plant uptake of Cd in leafy and root vegetables (UK Environment Agency 2002b):

**Leafy vegetables:** \[ Ln (CF) = 11.174 – 1.6461 \times \text{pH} \]  
\hspace{1cm} (2.2)

(UK Environment Agency 2002b)

**Root vegetables:** \[ Ln (CF) = 11.206 – 1.6340 \times \text{pH} \]  
\hspace{1cm} (2.3)

(UK Environment Agency 2002b)

Where CF is the soil to plant concentration factor and both of the concentrations are on a dry weight basis. Kim (2005) developed a contour diagram of Cd uptake by generic leafy home garden vegetables according to equations 2.2 and 2.3 (Figure 2.6).
Figure 2.6. Contour diagram of Cd uptake by generic leafy home garden vegetables (the moisture content of the plant was assumed to be 94%) (from Kim 2005)

Because bread is an important staple for New Zealanders, Cd concentrations in wheat should be assessed. Recommended total Cd concentrations in soils used for wheat production were developed to ensure that the Cd concentration in wheat does not exceed the standard of 0.1 mg kg\textsuperscript{-1} Cd (Table 2.10).
Table 2.10. The suggested maximum amount of Cd allowed in soils receiving biosolids to ensure the concentration of Cd in wheat grain does not exceed the standard value of 0.1 mg kg\(^{-1}\) wheat (from FSANZ 2005)

<table>
<thead>
<tr>
<th>pH</th>
<th>5</th>
<th>25</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>0.3</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>5.5</td>
<td>0.6</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>6.5</td>
<td>0.9</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>7.5</td>
<td>1.1</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>8.5</td>
<td>1.4</td>
<td>1.9</td>
<td>2.6</td>
</tr>
</tbody>
</table>

According to Kim (2005) about 1.5% of potatoes from the Waikato region exceeded the maximum amount of 1 mg kg\(^{-1}\) in 2004. Potato is among the crops that require high amounts of superphosphate fertilisers (about 800-1000 kg ha\(^{-1}\) yr\(^{-1}\)). Asparagus and apples also require high amounts of phosphate fertilisers (200-400 kg ha\(^{-1}\) yr\(^{-1}\) for asparagus and 100 kg ha\(^{-1}\) yr\(^{-1}\) for apple) (Mills et al. 2004).

### 2.6 Cadmium uptake by animals

Zinc is an essential element for animals and because of the strong similarity between the chemistry of Cd and Zn, Cd can enter metabolic pathways which need Zn (Kross et al. 1995). The main pathway of Cd uptake by animals is the accumulation of Cd in kidneys and livers of farm animals (Fitzgerald et al. 1985; Van Bruwaene et al. 1986). The control of the amount of Cd uptake by animals is important, because of its direct impact on human food consumption and also NZ offal export. However, the amount of Cd in animal milk and muscle is very low (Lee et al. 1994; Lee et al. 1996), therefore with the exception of offal consumption, the concern about Cd entry to the human diet through cattle...
products is low. The maximum permitted concentration of Cd in NZ food has changed since 2002 (Loganathan et al. 2008) (Table 2.11).

Table 2.11. The maximum permitted concentration of Cd in New Zealand food (from Furness 2001; Loganathan et al. 2008)

<table>
<thead>
<tr>
<th></th>
<th>Cadmium concentration in fresh weight (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kidneys</td>
<td>1</td>
</tr>
<tr>
<td>Liver</td>
<td>1</td>
</tr>
<tr>
<td>Meat flesh (muscle)</td>
<td>1</td>
</tr>
<tr>
<td>Leafy vegetables</td>
<td>1</td>
</tr>
<tr>
<td>Root and tuber vegetables</td>
<td>1</td>
</tr>
<tr>
<td>Wheat</td>
<td>1</td>
</tr>
</tbody>
</table>

The results of Solly et al. (1981) showed that Cd concentration exceeded the maximum tolerable amount of 1 mg kg\(^{-1}\) in about 5% of sheep, cattle and pig kidneys. About 22-28% of sheep and 14-20% of cattle kidneys in New Zealand exceed the permitted amount of 1 mg kg\(^{-1}\) from 1988 to 1991 (Roberts et al. 1994). Reiser et al. (2014) also showed that in 2.9% of cows’ kidney and also in 1.4% and 2.9% of sheep’s kidneys and livers, the concentration of Cd exceeded the maximum permitted value (2.5 mg kg\(^{-1}\) Cd for kidney and 1.25 mg kg\(^{-1}\) Cd for liver). The results of Reiser et al. (2014) showed that Cd intake from soil ingestion was less important than intake from pasture plants and forage in pasture systems. The main pathways of Cd in a pastoral system are shown in Figure 2.7.
2.7 Cadmium uptake by humans

Cadmium uptake from food is the main pathway of Cd entry to the non-smokers’ body (FAO/WHO 2010). Due to the absence of homeostatic control for Cd in the human body, Cd is toxic for humans and about one third of absorbed Cd is stored in the human kidney. In cases of high Cd ingestion, Cd\(^{2+}\) can replace Zn\(^{2+}\) in the human body at key enzyme sites causing metabolic disorders. Cadmium can also compete with Fe and Cu and causes the deficiency of these essential metals in the human body (Singh 2016). The World Health Organization (WHO) suggested that the maximum intake of Cd that can be tolerated by adults is 1 µg Cd kg\(^{-1}\) body day\(^{-1}\) (Fertiliser Matters 2010) or 7 µg Cd kg\(^{-1}\) body week\(^{-1}\) (Vannoort et al. 2000); MfE suggested the monthly maximum tolerable intake of 25 µg of Cd kg\(^{-1}\) body (MfE 2011). In 1995, only 6% of Cd entering the human diet originated from animal products in New Zealand (Vannoort et al. 1995) and recent research...
showed that the dietary intake of Cd in New Zealand is less than half of the tolerable amount of Cd for humans.

The residence time of Cd in the human kidney is approximately 15 years (WHO 2011) and the average residence time for Cd in the human body can be about 20 to 40 years (Nriagu 1980b).

The accumulation of Cd in the human body increases with age and varies from 1 µg at birth to about 15,000 to 80,000 µg for a 50-year-old person. The extent of Cd accumulation depends on the geographic locality and personal history (Venugopal & Luckey 1978; Kim 2005).

According to the New Zealand Total Diet Survey (NZTDS) by the Ministry of Agriculture and Forestry (MAF) in 2009 (MAF 2009), oyster made the highest contribution in dietary exposure of Cd for 25+ year males in New Zealand (MAF 2009; Figure 2.8).

Figure 2.8. Contribution of specific food groups to dietary exposure to cadmium (from MAF 2009)
Also, cocoa and some related products such as chocolate and chocolate biscuits are potential sources of Cd in NZ food (Stenhouse 1991). Therefore, according to the analysis of food in NZTDS, 74% of the weekly Cd exposure of the 25+ year male comes from five specific foods of the 121 different analyzed food types (Vannoort & Thomson 2005) and because of the high concentration of Cd in oysters, oyster consumption is recommended to be limited (Vannoort et al. 2000). In addition to agricultural technology, industrial activities and geological sources, food processing (such as food additives as well as physical and chemical contact with equipment and vessels) can result in Cd contamination in food (Adriano 2001).

The Provisional Tolerable Monthly Intake (PTMI) of 25 \( \mu \text{g Cd kg}^{-1} \) body (weekly intake of 7 \( \mu \text{g Cd kg}^{-1} \) body) was suggested by the World Health Organization (WHO). However, the European Food Safety Authority (EFSA) introduced the tolerable weekly intake value of 2.5 \( \mu \text{g kg}^{-1} \) body for Cd (Authority 2009). By comparison, Cd intake in New Zealanders is higher than a number of other countries (Figure 2.9); however, this intake was well below the PTMI by both WHO and EFSA standards (MAF 2009). The European Food Safety Authority (EFSA) points out that for vegetarians, smokers, children and people living in highly contaminated areas the maximum weekly intake of Cd may exceed this level by about 2-fold (Authority 2009).
The historical use of phosphate fertilisers originating from Nauru rocks and the acidity of NZ soils which enable higher plant uptake of Cd, have been suggested as two possible reasons for the higher intake of Cd by people in New Zealand in comparison to other countries (Kim 2005).

2.8 Analytical methods of soil digestion to measure Cd concentration

2.8.1 Total digestion

Different methods have been introduced to determine total or acid digestible concentration of metals including Cd:

- USEPA 3050B. A strong acid digestion method that can dissolve all the environmentally available elements. It is recommended that the samples digested in strong acid should be analysed by either Flame Atomic Absorption Spectrometry (FAAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Graphite Furnace Atomic Absorption
(GFAA) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For GFAA or ICP-MS analyses, HNO$_3$ and 30% H$_2$O$_2$ are suggested for soil digestion. For analyses by FLAA and ICP-AES, HCl is suggested for soil digestion (USEPA 1996a).

- **USEPA 3052.** A mixture of concentrated HNO$_3$ and concentrated HF has been suggested for soil digestion (USEPA 1996b).
- **Roberts *et al.* (1994) used a mixture of HClO$_4$ and HNO$_3$ to digest the soil samples.**
- **Gray *et al.* (1999b) introduced different methods to determine the total concentration of Cd. The USEPA SW 846-Method 3051 was employed for sample digestion. In this method, 69% Aristar grade HNO$_3$ was employed for sample digestion. Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) with a deuterium background correction was utilized to determine Cd concentration and 0.1% H$_3$PO$_4$ acid was the modifier. Another extraction method was Cd extraction using EDTA.**
- **McDowell (2010) used HNO$_3$ to digest soil samples and Inductively Coupled Plasma Emission Mass Spectrometry (ICP-MS) to measure the concentration of Cd (McDowell 2010).**
- **Aqua Regia is a 1:3 (by volume) mixture of HCl and HNO$_3$ and has been widely used to digest the soil samples to measure the concentration of metals including Cd (Loganathan *et al.* 1996; Cadmium Working Group 2008; Taylor & Kim 2009; Reiser *et al.* 2014).**

Soil samples were digested by using Aqua Regia in this study.
2.8.2 Sequential extraction

- Tessier *et al.* (1979) introduced a sequential method, which provides the metal separation in five general fractions:
  - Exchangeable: soil sample is extracted at room temperature for 1 h with 8 mL of 1M MgCl₂ (pH 7) with continuous agitation.
  - Bound to carbonates: The residue from first step is digested with 8 mL of 1.0 M sodium acetate (adjusted to pH 5 with acetic acid) at room temperature. The mixture is shaken for 5 h.
  - Bound to Fe–Mn oxides: The residue obtained from the second step is refluxed at 96 ± 3 °C with 20 mL of 0.04 M NH₂OH. HCl in 25% (v/v) acetic acid or 20 mL of 0.3 M Na₂S₂O₄ + 0.175 M Na-citrate or 0.04 M NH₂OH.HCl in 25% (v/v) HOAc for 6 h.
  - Bound to organic matter: 3 mL of 0.02M HNO₃ and 5 mL of 30% H₂O₂ should be added to the residue obtained from third step and pH is adjusted to 2 with HNO₃. The mixture is refluxed at 85 ± 2 °C for 2 h. 3 mL aliquot of 30% H₂O₂ (pH 2 with HNO₃) is again added to the sample being refluxed for 3 h at 85 ± 2 °C. After cooling, 5 mL of 3.2 M ammonium acetate in 20% (v/v) HNO₃ should be added. The sample should be diluted to 20 ml and shaken continuously for 30 min.
  - Residual: The residue obtained from forth step is digested with HF-HCLO₄ to extract the heavy metals (here Cd).

Between each extraction, the samples should be centrifuged at 10000 rpm for 30 minutes.
Tessier’s method was followed (except for using Aqua Regia for the last fraction) to determine the Cd speciation of the soils studied herein.

### 2.9 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the concentration of metals in soil and fertiliser samples. ICP-MS can measure the concentration of metal and several non-metals with a better detection limit for most elements, higher sensitivity and speed compared to Atomic Absorption (Thomas 2003). ICP-MS is a combination of a high temperature ICP source and a mass spectrometer. When the sample is introduced to ICP-MS, it is ionized in the ICP, which is a plasma generated by inductively heating the carrier gas using an electromagnetic coil. Then the ions are accelerated into the mass spectrometer through a series of cones (usually a quadrupole). The ions then can be separated based on their mass-to-charge ratio and the detector can receive the ion signal proportional to the concentration (Figure 2.10) (Thomas 2003).

![Figure 2.10. Schematic diagram of ICP-MS (from Thomas 2003)](image)

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2.10 Cadmium isotope analysis

Stable isotope ratio analysis is a tool to trace the sources of metals in the environment and is increasingly applied in studies of the origin and history of heavy metals in the environment (Gao et al. 2013; Arendt et al. 2015; Félix et al. 2015; Wiederhold et al. 2015). Isotopic ‘fingerprints’ help to trace the sources of elements, the fractional contribution of different sources and their fate. For example, Cloquet et al. (2006) studied samples from a refinery plant in France and, using Cd isotope compositions, they found three major sources (dust, slag and agricultural soil) for Cd in the refinery plant and the contribution of different sources was estimated to be about 65% for dust, about 25% (maximum of 80% for one sample) for slag and less than 10% for agricultural reference topsoil. Therefore dust was the main source of Cd in the sampling location.

Cadmium has eight stable isotopes including $^{106}$Cd (1.3%), $^{108}$Cd (0.9%), $^{110}$Cd (12.5%), $^{111}$Cd (12.8%), $^{112}$Cd (24.1%), $^{113}$Cd (12.2%), $^{114}$Cd (28.7%) and $^{116}$Cd (7.5%) (Wombacher & Rehkämper 2004). This large number of isotopes increases the power of isotopic studies of Cd. In most geochemical studies, the Cd stable isotope ratio of $^{114}$Cd/$^{110}$Cd has been used to facilitate inter-laboratory comparisons (Wombacher & Rehkämper 2004).

2.10.1 MC-ICPMS

MC-ICPMS (Multicollector-Inductively Coupled Plasma Mass Spectrometer) and TIMS (Thermal Ionisation Mass Spectrometry) are two common instruments used to measure the isotope ratios of elements such as Cd. MC-ICPMS is more common than TIMS, as MC-ICPMS gives a more precise determination of isotopic compositions with high ionization potentials.
(Rehkämper et al. 2001). The technique of MC-ICPMS was developed to improve the precision of ICP-MS. Conventional ICP-MS consists of a quadrupole analyser, which is only capable of single-collector analysis, and therefore limits the precision of ICP-MS to about 1%, which is insufficient for isotope systems. MC-ICPMS is a combination of an ICP plasma source with an energy filter, a magnetic sector analyser, and multiple Faraday collectors. After sample ionization in the ICP, the ions pass through the energy filter (to produce a consistent energy spectrum) and then through a magnetic field in which the ions are separated based on their mass-to-charge ratio. Then the ions are directed into collectors to convert to a voltage, so the isotope ratios can be calculated by comparing the voltages from different collectors (Figure 2.11). The excellent sensitivity, high ionization efficiency, and high precision due to multiple ion beam collection associated with MC-ICPMS have allowed the determination of Cd isotopes with high level of precision ($\varepsilon$-level) (Rehkämper et al. 2001).

Figure 2.11. Schematic diagram of Nu Plasma (Nu Instruments) MC-ICPMS (from Rehkämper et al. 2001)
2.10.2 Fractionation correction

Large isotopic fractionation (mass bias) can happen in MC-ICPMS (Rehkämper et al. 2004) during ion extraction within the plasma and transport to the mass spectrometer and therefore lighter isotopes are lost to a greater degree (< 1% of ions can be extracted through the skimmer cone) (Andren et al. 2004; Gault-Ringold 2011). The magnitude of this fractionation is usually ten times greater than the natural fractionation of the isotope. However, because of the relatively constant and non-time dependent fractionation, this fractionation can be corrected (Rehkämper et al. 2004). There are three common ways of fractionation correction:

2.10.2.1 Sample standard bracketing (SSB)

In this method, a matrix matched isotopic standard is run before and after the sample. The instrumental mass bias factor is then calculated using the difference of the real and measured isotopic compositions of the standard. The isotopic composition of the sample can then be corrected using linear interpolation of the instrumental mass bias factors (Gault-Ringold & Stirling 2012).

2.10.2.2 External normalization

External normalization can be conducted alone or in combination with SSB. Because instrumental mass fractionation is dependent on mass, not on chemical nature of the analyte, in an overlapping mass range, the mass bias behavior of one element can be used to characterize the mass bias behavior of another (such as Ag for Cd and Zn for Cu). The assumption is that the
standard element and the target element show the same fractionation pattern in the instrument. In this method, isotope fractionation of both sample and standard can be corrected using the correction factor of the standard element. This method is usually recommended for elements with less than four isotopes (Gault-Ringold 2011).

2.10.2.3 Double spike (DS) technique

The double spike (DS) technique is a method of internal normalization which is recommended for elements with more than four isotopes such as Cd. Rudge et al. (2009) defined the double spike method as the measurement of the relative amounts of four isotopes “two of which are enhanced by the addition of enriched isotopic spikes to the sample”. This method is now being introduced as the most accurate type of mass bias correction, because it allows for mass bias correction during the same run as the sample. Interpolation on the basis of the standard measurement is not required in this method, and therefore the time-dependence of changes of the instrument mass fractionation is eliminated. The spike is added to the sample before sample chemical processing and it involves of spiking the samples with a known solution which is enriched in two isotopes of the corresponding element relative to the natural abundance of the isotope (Rehkämper et al. 2011).
2.10.3  Cadmium isotopic standards

2.10.3.1  Isotope notation

There are two common methods of notation for reporting isotope ratios of $^{114}\text{Cd}/^{110}\text{Cd}$:

$$\delta^{114/110}\text{Cd} = \left[ \frac{\left( ^{114}\text{Cd}/^{110}\text{Cd}\right)_\text{sample}}{\left( ^{114}\text{Cd}/^{110}\text{Cd}\right)_\text{standard}} - 1 \right] \times 1000$$  (2.4)

$$\epsilon^{114/110}\text{Cd} = \left[ \frac{\left( ^{114}\text{Cd}/^{110}\text{Cd}\right)_\text{sample}}{\left( ^{114}\text{Cd}/^{110}\text{Cd}\right)_\text{standard}} - 1 \right] \times 10,000$$  (2.5)

Where $\left( ^{114}\text{Cd}/^{110}\text{Cd}\right)_\text{sample}$ refers to the isotope ratios of the sample or the standard. $\epsilon$ is more sensitive than $\delta$ (by a factor of 10).

2.10.3.2  Standard isotope compositions

As can be seen in equations 2.4 and 2.5, the isotope ratio of the sample is reported relative to the isotope ratio of a standard (or a reference material). A variety of reference materials are used for Cd isotope evaluations (Table 2.12) (Rehkämper et al. 2011).
Table 2.12. The isotope ratios of Cd ($^{114/110}\text{Cd} \pm 2\text{SD}$) from various intercalibration standards by different laboratories and techniques (from Rehkämper *et al.* 2011 and Abouchami *et al.* 2013)*

<table>
<thead>
<tr>
<th>Methods and instrument</th>
<th>BAM-I012Cd</th>
<th>Münster Cd</th>
<th>Alfa Cd (Zürich)</th>
<th>MPI JMC Cd</th>
<th>NIST 3108 Cd</th>
<th>NZ JMC Cd</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-n³, MC-ICPMS</td>
<td>-10.8 ± 1.5</td>
<td>46.5 ± 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Wombacher &amp; Rehkämper 2004)</td>
</tr>
<tr>
<td>SSB⁵, MC-ICPMS</td>
<td></td>
<td>44.3 ± 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Cloquet <em>et al.</em> 2005)</td>
</tr>
<tr>
<td>Ag-n, MC-ICPMS</td>
<td></td>
<td>44.3 ± 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lacan <em>et al.</em> 2006)</td>
</tr>
<tr>
<td>DS², MC-ICPMS</td>
<td>-12.4 ± 1.1</td>
<td>46.4 ± 1.2</td>
<td>0.0 ± 0.5</td>
<td></td>
<td></td>
<td></td>
<td>(Ripperger &amp; Rehkämper 2007)</td>
</tr>
<tr>
<td>Ag-n, MC-ICPMS</td>
<td>-11.4 ± 1.5</td>
<td>46.0 ± 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Ripperger &amp; Rehkämper 2007)</td>
</tr>
<tr>
<td>DS, TIMS</td>
<td>-12.3 ± 0.3</td>
<td>44.8 ± 0.2</td>
<td>2.2 ± 0.2</td>
<td></td>
<td></td>
<td></td>
<td>(Schmitt <em>et al.</em> 2009a; Schmitt <em>et al.</em> 2009b)</td>
</tr>
<tr>
<td>SSB, MC-ICPMS</td>
<td>-12.0 ± 1.2</td>
<td>45.9 ± 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Gao <em>et al.</em> 2008)</td>
</tr>
<tr>
<td>Ag-n, MC-ICPMS</td>
<td>-13.7 ± 2.5</td>
<td>45.0 ± 0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Shiel <em>et al.</em> 2009)</td>
</tr>
<tr>
<td>DS, MC-ICPMS</td>
<td></td>
<td>0.5 ± 0.4</td>
<td>2.6 ± 0.4</td>
<td></td>
<td></td>
<td></td>
<td>(Horner <em>et al.</em> 2010)</td>
</tr>
<tr>
<td>DS, MC-ICPMS</td>
<td>-13.1 ± 1.4</td>
<td>45.1 ± 1.3</td>
<td>0.0 ± 0.9 -16.2 ± 1.1</td>
<td></td>
<td></td>
<td></td>
<td>(Gault-Ringold <em>et al.</em> 2012)</td>
</tr>
<tr>
<td>DS, MC-ICPMS</td>
<td>-12.4 ± 0.7</td>
<td>46.2 ± 0.5</td>
<td>0.5 ± 0.5</td>
<td>1.0 ± 0.2</td>
<td></td>
<td></td>
<td>(Xue <em>et al.</em> 2012)</td>
</tr>
</tbody>
</table>

* Note the references in the table were sourced by Rehkämper *et al.* 2011 and Abouchami *et al.* 2013

³ Ag-n: Ag normalization
⁵ SSB: standard-sample bracketing
² DS: double spike

In this research, NIST3108 was used as the reference material.
2.11 Summary and conclusion

According to an extensive literature review, authors have reported contrasting conclusions relating to the distribution and behaviour of Cd in different soils (Roberts et al. 1994; Zanders 1998; Stafford et al. 2015) and it is not clear whether different soils accumulate Cd at similar rates under same P loadings. However, in most of the previous studies, the fertiliser history was unknown or was not the same between various soil types. Therefore, to address this gap in the literature, for the first part of this research, three contrasting soils were selected to assess whether Cd distributions differed between contrasting soils. All three soil types were from the same paddock to ensure that they had the same fertiliser history and thus the same Cd input.

As is mentioned in the literature review, the main source of phosphate fertilisers in New Zealand has changed since 1997 from Nauru rock phosphate to a variety of other rock phosphates with lower amounts of Cd. The accumulation trend of Cd in Winchmore research farm showed a plateau around the same time (about 2000) (McDowell 2012). This research questions how the change in fertiliser sources affected the soil Cd, what is the fraction distribution of Cd, and can we distinguish the different sources of Cd? Therefore, the Cd stable isotope ratio ($\delta^{114/110}$Cd) technique was employed to assess whether we can trace the sources of Cd in NZ soils through time and distinguish the contribution of different sources of Cd in NZ soils.

According to the literature review, there were contrasting conclusions on the potential for mobility/leaching of Cd. While some research has shown minor mobility and/or leaching for Cd, a number of other studies found significant translocation of Cd through the soil profile (Loganathan & Hedley 1997; Gray et
al. 2003b). This research also seeks to answer to how Cd is mobilised or translocating in soil. Therefore, the last part of this thesis addressed the comparison of the mobility (or loss) of Cd between irrigated and unirrigated soils with the same fertiliser history and thus the same Cd input through time.
References


observations', *Journal of Analytical Atomic Spectrometry*, vol. 19, no. 9, pp. 1217-1224.


Bolan, N. S., Adriano, D. C. & Naidu, R. 2003, 'Role of phosphorus in (Im)mobilization and bioavailability of heavy metals in the soil-plant system', *Reviews of Environmental Contamination and Toxicology*, vol. 177, pp. 1-44.


Cloquet, C., Rouxel, O., Cargignan, J. & Libourel, G. 2005, 'Natural cadmium isotopic variations in eight geological reference materials (NIST SRM 27 11, BCR 176, GSS-1, GXR-1, GXR-2, GSD-12, Nod-P -1, Nod-A-1) and anthropogenic samples, measured by MC-ICP-MS', *Geostandards and Geoanalytical Research*, vol. 29, pp. 95-106.


FAO/WHO (Food and Agriculture Organisation/World Health Organisation) 2010, 

*Summary and conclusion*, Joint FAO/WHO Expert Committee on Food Additives, 73rd meeting, Geneva, Switzerland.


Furness, H. 1998, *Legal, recommended or voluntary levels of cadmium in superphosphate. compiled from a number of reported studies*, Fertilizer Research, New Zealand.


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:


metalloid contamination of agricultural land in Australia and New Zealand',

*Soil Research*, vol. 38, no. 6, pp. 1037-1086.


management for the farm, catchment and community, Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand.


Thomas, R. 2003, *Practical guide to ICP-MS: A tutorial for beginners*, CRC Press, USA.


UK Environment Agency 2002b, *Soil guideline values for cadmium accumulation*, Department for Environmental, Food and Rural Affairs (DEFRA), UK.


sweet corn, and wheat', *Journal of Agricultural and Food Chemistry*, pp. 1240-1244.


Chapter 3. Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history

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Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history

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ABSTRACT
Cadmium (Cd) concentration in New Zealand (NZ) agricultural soils has increased due to phosphate fertilizer application, but it is not clear whether soils with different properties accumulate Cd at similar rates for given P loadings. Here, the distribution of Cd was measured in three soils: the well-drained Horotiu series (Orthic Allophanic Soil in NZ soil classification, Typic Hapludand in US soil taxonomy), poorly-drained Te Kowhai series (Orthic Gley Soil in NZ classification, Typic Humaquept in US soil taxonomy) and an intergrade between them, Brunwood series (Impeded Allophanic Soil in NZ soil classification, Aquic Hapludand in US soil taxonomy). All three soils often occur in the same paddock with the same fertilizer history, but have differing drainage and mineralogical characteristics, permitting an assessment of the potential for varying accumulation/translocation of Cd in contrasting soil conditions. Thirty soil profiles from ten paddocks on a dairy farm near Hamilton, NZ, with a uniform fertilizer history were sampled to depth of 60 cm. The Cd concentration in topsoil (0–7.5 cm) samples (mean of 0.79 mg kg⁻¹) was about 7–8 times greater than in deeper horizons (P < 0.001). No significant differences in Cd concentration or fractionation among the soil series were detected. Cluster analysis showed that Cd, phosphorus (P) and uranium (U) were highly correlated, consistent with a common source, most likely phosphate fertilizer. The absence of a difference in the Cd depth profiles in the three soils indicates that Cd was preferentially adsorbed to the topsoil and was not significantly mobilized by drainage in the soils. The lack of difference in Cd distribution between contrasting soil series supports the use of one Cd management system tool for all of these soils.

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1. Introduction
Cadmium (Cd) is a biotoxic heavy metal which can be adsorbed by soils and then bioaccumulated by plants, animals, and humans (McLaughlin and Singh, 1999). Although many anthropogenic sources of Cd exist, the greatest source of Cd in New Zealand (NZ) soils is phosphate fertilizer (Gray et al., 1999; Loganathan et al., 2003; Schipper et al., 2011; McDowell, 2012). Accumulation of Cd was first highlighted in NZ by reports of Cd bioaccumulation in the kidneys and livers of grazing animals (Lee et al., 1994; Loganathan et al., 2008). The concentration of Cd in NZ agricultural soils has increased especially in the Waikato region where dairy farms predominate and fertilizer is applied at higher rates than drystock farms (Taylor et al., 2007; Stafford et al., 2014). Thus, Cd is one of the most important contaminants in NZ soils because of its widespread accumulation and long-term impact (Gaw et al., 2006). Like Cd, uranium (U) in New Zealand soils is mainly derived from phosphate fertilizer and there is also concern about its increasing concentration and therefore potential toxicity (Schipper et al., 2011).

Prior to 1997 phosphate fertilizers used in New Zealand were mainly produced from Nauru Island phosphate rocks (mean of 450 mg Cd/kg P in fertilizer). Since 1997, the main source of NZ phosphate fertilizers has been changed to phosphate rocks with lower concentrations of Cd and the fertilizer industry has elected to produce phosphate fertilizers with ~280 mg Cd/kg P. However, the maximum permissible amount of Cd in NZ phosphate fertilizers remains high relative to phosphate fertilizers produced internationally (Furness, 1998; Oosterhuis et al., 2000).

Research on the amount of Cd in soils of New Zealand (Roberts et al., 1994; Andrews et al., 1996; Gray et al., 2003; Longhurst, 2006; McDowell et al., 2013) and other countries (Holmgren et al., 1993; Holm et al., 1998; Holm et al., 2003; Karimi Nezhad et al., 2014) has generally lacked detailed information on the fertilizer history of sample sites. Site fertilizer history is important to explain trends in Cd accumulation. Cd adsorption has been proposed to vary between soils due to differences in particle size, pH, organic matter content, and abundance of mineral phases able to undergo adsorption/desorption reactions with metal cations (Naidu et al., 1994; Gray et al., 1999). For instance, Cd adsorption has been shown to be greater in Allophanic Soils than in non-Allophanic Soils (Bolan et al., 2003, 2013) implying that soil...
mineralogy directly contributes to Cd retention. Bolan et al. (2013) showed that there were more surface negative charges in Allophanic Soils than non-Allophanic Soils and that allophanic clay therefore may be one of the reasons for higher Cd adsorption in Allophanic Soils. Bolan et al. (2003) also showed that phosphate addition to soils increases the soil pH, negative charge, and therefore Cd adsorption and the Allophanic Soils have greater increases in Cd adsorption than non-Allophanic Soils. Parfitt (1992) and Yuan and Wada (2012) also stated that allophane has an appreciable amount of variable negative and positive charges and therefore can absorb both cations (such as Cd) and anions.

Past workers have attempted to examine the effect of soil type on Cd accumulation trends. Roberts et al. (1994) determined the concentration of Cd in native and pastoral soils (0–7.5 cm) on eight soil types in New Zealand with varying land uses. The results showed that the mean concentration of Cd in the native (non-agricultural) Allophanic Soils and Gley Soils was not significantly different. The mean concentration of Cd varied between different Soil Orders under pastoral agriculture and the Cd concentration in topsoils of Allophanic Soils was more than non-Allophanic Soils (Roberts et al., 1994). However, Roberts et al. (1994) were not able to separate the effects of fertilizer history on soil Cd differences between Soil Orders because some Soils Orders

### Table 1

<table>
<thead>
<tr>
<th>Rate (kg ha⁻¹)</th>
<th>Product</th>
<th>% Superphosphate</th>
<th>Rate of Superphosphate (kg ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autumn 2000</td>
<td>650</td>
<td>Magnesium phosphate + (Selenium @ 1 kg ton⁻¹)</td>
<td>92% 598</td>
</tr>
<tr>
<td>Autumn 2001</td>
<td>700</td>
<td>Magnesium phosphate + (Selenium @ 1 kg ton⁻¹)</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2002</td>
<td>650</td>
<td>Magnesium phosphate + (Selenium @ 1 kg ton⁻¹)</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2003</td>
<td>600</td>
<td>Magnesium phosphate</td>
<td>83% 523</td>
</tr>
<tr>
<td>Autumn 2004</td>
<td>650</td>
<td>92% Superten + 8% Calcined Magnesite (CalMag)</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2005</td>
<td>570</td>
<td>91% Superten + 4% Durasul Sulphur + 5% CalMag + 1 kg ha⁻¹ Selcote Ultra</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2006</td>
<td>630</td>
<td>91% Superten + 3% Durasul Sulphur + 5% CalMag + 1 kg ha⁻¹ Selcote Ultra (1% Selenium)</td>
<td>83% 523</td>
</tr>
<tr>
<td>Autumn 2007</td>
<td>570</td>
<td>83% Superten + 8% Salt + 5% CalMag + 5% Durasul</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2008</td>
<td>570</td>
<td>91% Superten + 5% Salt + 4% CalMag</td>
<td>91% 519</td>
</tr>
<tr>
<td>Autumn 2009</td>
<td>675</td>
<td>77% Superten + 8% Muriate of Potash + 7% Salt + 3% CalMag + 4% Durasul</td>
<td>77% 520</td>
</tr>
<tr>
<td>Autumn 2010</td>
<td>635</td>
<td>87% Superten + 8% Bulk Salt + 5% CalMag</td>
<td>87% 552</td>
</tr>
<tr>
<td>Autumn 2011</td>
<td>675</td>
<td>77% Superten + 8% Muriate of Potash + 7% Salt + 3% CalMag + 4% Durasul</td>
<td>77% 520</td>
</tr>
<tr>
<td>Autumn 2012</td>
<td>615</td>
<td>11% Superten + 81% Serpentine Super + 8% Summit Agricultural Salt (AgSalt) mix</td>
<td>11% 68</td>
</tr>
<tr>
<td>Autumn 2013</td>
<td>675</td>
<td>41% Superten + 82% Serpentine super + 7% AgSalt mix</td>
<td>41% 277</td>
</tr>
<tr>
<td>Autumn 2014</td>
<td>600</td>
<td>50% Serpentine Super + 50% Superten + 1 kg Selenium ha⁻¹</td>
<td>50% 300</td>
</tr>
</tbody>
</table>
were generally more intensively farmed, and thus had higher fertilizer inputs, than others. Zanders (1998) reported that 13% of variation in Cd concentration in NZ soils was explained by soil group, and at the farm scale, soil parent material was not a primary determinant of Cd distribution among different soil types. However, Stafford et al. (2015) showed that at the farm scale the Cd concentration in Gley Soils was significantly lower ($P < 0.001$) than Allophonic Soils with the same fertilizer history.

Any assessment of Cd accumulation in different soils from P fertilizer inputs must first estimate the amount of Cd that would occur naturally from parent material. A correlative approach has been recently proposed to determine the natural Cd background and anthropogenic Cd concentration in NZ soils (McDowell et al., 2013). These authors used two data sets including 11 soil orders, and background sites from soils sampled under native forest. The anthropogenic sites were from soils under varying land uses including arable, dairy, and drystock farming, horticulture, forestry, and urban development. A linear regression based on the relationship between Cd and P in background soil samples (Eq. (1)) was used to predict the maximum concentration of background Cd in soils under various land-uses and showed no significant differences in predicted concentration of background Cd between different soils (McDowell et al., 2013).

$$\text{Cd} = 0.000142 \text{ total P} + 0.042$$  

(where Cd and P are concentrations in mg kg$^{-1}$).

The approach of McDowell et al. (2013) was developed to estimate the maximum possible background level of Cd in NZ human-influenced soils. However, Simmler (2013) suggested that this approach was limited because it is likely to over-estimate the background concentration of Cd (Simmler, 2013).

In response to growing concern regarding the steady accumulation of Cd in NZ soils, the New Zealand Cadmium Working Group introduced the “Tiered Fertilizer Management System” (TFMS) to manage Cd concentration in NZ soils and identified five tiers based on Cd concentrations in soil and defined different management tools for each tier (MAF, 2011a):

- Tier 0: Cd concentration $< 0.6$ mg kg$^{-1}$, no limitation on the phosphate fertilizer application is considered however a five-yearly screening soil test is required to check the status of Cd
- Tier 1: $0.6 \leq$ Cd concentration $< 1.0$ mg kg$^{-1}$, restriction on the products and application rates to minimize the accumulation of Cd, and also using approved programs to test the concentration of Cd every five years
- Tier 2: $1 \leq$ Cd concentration $< 1.4$ mg kg$^{-1}$, a Cd balance program is required to manage the application rates of Cd to ensure that the concentration of Cd does not exceed the acceptable threshold (tier 4) in the next 100 years
- Tier 3: $1.4 \leq$ Cd concentration $< 1.8$ mg kg$^{-1}$, a Cd balance program is required to manage the application rates of Cd to ensure that the concentration of Cd does not exceed the acceptable threshold (tier 4) in the next 100 years. Farms with Cd concentration in this category need to receive the absolute minimum amount of phosphate fertilizer during the interim seven year period. Therefore the rate of fertilizer application as well as choice of phosphate fertilizers are further restricted (MAF, 2011b; Sneath, 2015).
- Tier 4: Cd concentration $\geq 1.8$ mg kg$^{-1}$, no further accumulation of Cd allowed.

An implicit assumption underlying the TFMS approach to Cd management was that all soils accumulate Cd at similar rates. This is potentially problematic, as different soils may have varying capacities to hold Cd or release Cd, either to plant uptake or to moving deeper into the soil.

The Zn/Cd ratio has been widely used in soil Cd studies because Zn and Cd have similar chemical properties (Swaine, 1962; Roberts et al., 1994; Zanders et al., 1999) and thus tend to concentrate to similar extents in natural materials. Hooda (2010) suggested that both Cd and Zn should be considered in any assessment of Cd accumulation in soils. A lower Zn/Cd ratio in anthropogenically-impacted soils (compared to native soils) is expected in soils contaminated by fertilizers containing a greater concentration of Cd than Zn. However, Zn also enters NZ pastoral soils via animal health remedies (Gaw et al., 2006).

One step toward understanding Cd accumulation trends is to develop data on Cd distribution in soils with varying properties but under the same P fertilizer loading.

The objective of our research was to determine if the distribution of Cd varies between soils with contrasting mineralogy and drainage characteristics, but the same P fertilizer history. For this research, we utilized a research farm with known P fertilizer history, but within which, soils of greatly contrasting mineralogy and drainage characteristics occur in the same paddock within 20 m of one another. This allowed us to compare Cd accumulation in contrasting soils with the same management history.
2. Materials and methods

2.1. Study area, sample collection and preparation

Soil samples were taken at Scott Farm (Table S1), a dairy farm, near Hamilton, NZ. Two contrasting soils (Horotiu and Te Kowhai) and an intermediate between them (Bruntwood) were selected (Fig. 1). All three soils often occur in the same paddock, so have the same fertilizer history. The Horotiu soil (Orthic Allophanic Soil in NZ classification, Typic Hapludand in US Soil Taxonomy) is an allophanic, well-drained soil and does not have any slowly permeable layer. The Te Kowhai soil (Orthic Gley Soil in NZ classification and Typic Humaquert in US Soil Taxonomy) is a halloysitic and poorly drained soil with a slowly permeable subsoil. The Bruntwood soil (Impeded Allophanic Soil in NZ classification and Aquic Hapludand in US Soil Taxonomy) is an intermediate between the Horotiu and Te Kowhai soils, which has allophanic surface horizons similar to Horotiu, while the lower subsoil contains a slowly permeable horizon similar to the Te Kowhai soil. Usually the Horotiu soil is formed in micro topographical rises, and the Te Kowhai in low-lying hollows. The Bruntwood soil is found between them (Singleton et al., 1989).

In addition to differences in drainage properties, the three soils have varying physical properties (Table S1). The soils are also distinguished on the basis of chemical properties such as cation exchange capacity (CEC), clay mineral content, and organic matter content (Singleton, 1991). The percentage of allophane in the clay minerals of the Horotiu soil is greater than in the Bruntwood soil, and allophane is absent or very low in the clay mineral fraction of Te Kowhai soils in which halloysite is the dominant clay mineral (Singleton et al., 1989; Lowe, 2010). For the same pH, the CEC in the Horotiu soil would be expected to exceed the CEC of the Te Kowhai soil, because the Horotiu soil contains more allophane which has a variable charge (Carroll, 1959; Petruzelli et al., 1985; Bolan et al., 2003; Itami and Yanai, 2006).

Ten paddocks with a known fertilizer history (Table 1) were selected for sampling and within each paddock, areas of Horotiu, Bruntwood and Te Kowhai soils were identified.

In each soil, a 60 cm deep pit was dug and soil horizons and textures were determined. Six soil depths were sampled. The first two depths were 0–7.5 cm (the recommended standard pasture topsoil sampling depth in NZ (Roberts et al., 1994)) and 7.5–15 cm. Deeper samples were taken from within each soil horizon (to a depth of 60 cm, Table S1). Soil samples from each depth were taken from three different sides of the pit and then bulked together. Also, soil dry bulk density samples (three replicate samples from each soil depth in each profile) were taken following Gradwell (1972). Visible vegetation was removed.
from the soil surface and the samples were transferred to the laboratory in plastic bags.

2.2. Soil properties

The soil samples were air dried (50 °C) and sieved using a 2 mm sieve. Then approximately 0.5 g of sample was weighed into a clean 50 ml Falcon tube. Soil was digested and analyzed using the method of Schipper et al. (2011) with some modifications. Aqua regia (1 ml HNO3 and 0.33 ml HCl) was added and left to pre-digest overnight on a digestion block with lids loose to prevent frothing. The samples were then digested at 50 °C for 1 h. After digestion, 50 ml of deionized water was pipetted into each digestion tube and the tubes were then centrifuged for 10 min at 4000 rpm and filtered at 0.45 µm (Schipper et al., 2011). The concentrations of Cd, phosphorus (P), zinc (Zn), copper (Cu), cobalt (Co), iron (Fe), manganese (Mn), uranium (U), arsenic (As), vanadium (V), and lead (Pb) were determined by quadrupole ICP-MS (Waltham, MA, USA) following calibration using NIST-traceable standards (Inorganic Ventures, Christiansburg, VA, USA). The soil pH was determined following Blakemore et al. (1987) using a Jenway pH meter (Stafford, UK). The soil dry bulk density samples were oven dried for 36 h (105 °C) and weighed. The mean of three soil dry bulk density replicates was reported. After determining the total concentration of Cd in different soils, fifteen topsoil (0–7.5 cm) samples from five paddocks across the full range of Cd concentrations encountered, were selected to assess the distribution of Cd in different operationally-derived fractions following Tessier et al. (1979). Because organic matter content and mineral phases affect the absorption behavior of Cd to soil (Naidu et al., 1994; Gray et al., 1999), the sequential extraction was applied to check the fractionation pattern of Cd in different fractions including exchangeable, bound to carbonate, bound to Fe and Mn oxides, bound to organic matter and residual. All the materials used for the sequential experiment were the same as in Tessier’s method except for the last (residual) fraction, which instead used an aqua regia digest.

2.3. Data analysis

The MVSP software package (Kovach Computing Services, 1993) was employed for cluster analyses. Cluster Analysis, based on Pearson’s correlation coefficients, was used to identify the relationship between element concentrations and the pH of the soil samples.

3. Results

Site locations, sample depth, soil types, horizon names, soil texture and Cd, P and U concentrations are included in the supplementary material (Table S1).

3.1. Total concentration of cadmium

The concentration of Cd in the A horizon of each soil was greater than deeper horizons (P < 0.001) (Fig. 2). The mean concentration of Cd in topsoil (0–7.5 cm) samples were 0.77 mg kg⁻¹ (range 0.56–0.99) in the Horotiu soil, 0.83 mg kg⁻¹ (0.60–1.11) in the Bruntwood soil and 0.78 mg kg⁻¹ (0.46–0.96) in the Te Kowhai soil. Eq. (1) was used to estimate the maximum background amount of Cd in the soils (Fig. 2). There were no significant differences in Cd concentration among the three soil series (Fig. 2).

The Cd concentrations in surface soils, were about 7–8 times greater than in subsoil samples (Fig. 2) and the concentrations of P, Cd, U, and Zn in the surface soils were also greater than reported background soils (Table 2). The other elements investigated were within the natural background concentration ranges.

There were no significant differences in pH among the different soil series. The mean pH (Table 2) was 5.8 (range 5.1–6.4) for the Horotiu soil, 5.7 (range 4.8–6.5) for the Bruntwood soil and 5.8 (range 5.2–6.4) for the Te Kowhai soil.

There were no significant differences in the total mass of Cd to 60 cm depth (calculated using the soil dry bulk density) among the three soil series (Fig. 3).

3.2. Sequential extraction method

The Cd fractionation in all the soil samples followed the same order: Fe-Mn oxides > exchangeable > bound to organic matter > bound to carbonates ≈ residual (Table 3).

3.3. Trace element ratio analysis

Zn/Cd ratios in the topsoil (0–7.5 cm) (99 for Horotiu, 95 for Bruntwood and 90 for Te Kowhai) were lower than the Zn/Cd ratios of NZ native topsoils (475 for Allophanic Soils and 760 for Gley Soils) and national pasture topsoils (179 for Allophanic Soils and 268 for Gley Soils) (Roberts et al., 1994). Also, the Zn/Cd ratio decreased with soil depth.

U/P, U/Cd and Cd/P ratios were calculated after normalizing the amount of U, Cd and P to the maximum value of these elements in each soil type of each paddock (Table S1, Fig. 4). The ratio of U/Cd and U/P were also examined on the basis that both U and P are derived from phosphate fertilizers, but can be predicted to have different mobilities on the basis that orthophosphate (present mainly as H2PO4⁻ at pH ~ 5.8) adsorbs strongly to allophane, whereas U (which mainly presents as UO2(CO3)2⁻ at pH ~ 5.8) is generally more soluble.

The U/Cd ratio increased with increasing soil depth for all soil types following the order Bruntwood > Te Kowhai > Horotiu (Fig. 4a). The relationship between U and P and also Cd and P were more distinct than U and Cd (Fig. 4b and c). The U/P and Cd/P ratios mostly increased with depth in both the Bruntwood and Te Kowhai soils, but were nearly constant with depth in the Horotiu soil (Fig. 4b and c).

3.4. Correlations between elements

Cluster analysis of trace elements based on Pearson’s correlation coefficient showed that Cd was highly correlated with U and P (Fig. 5). Based on the known association of U, Cd and P with fertilizer, cluster A represents phosphate fertilizer-derived elements. Cluster B contains Mn, Co, Cu and Zn and shows a significant correlation with cluster A. Additionally, significantly positive correlation coefficients were found between P and some other elements including Cu and Zn (Table 4).

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Mean of Cd concentration (mg kg⁻¹) in different fractions of topsoil (0–7.5 cm) samples from Horotiu, Bruntwood and Te Kowhai soil.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>Bound to carbonates</td>
</tr>
<tr>
<td>Horotiu</td>
<td>0.20</td>
</tr>
<tr>
<td>Bruntwood</td>
<td>0.20</td>
</tr>
<tr>
<td>Te Kowhai</td>
<td>0.20</td>
</tr>
</tbody>
</table>
4. Discussion

The total concentration of Cd in all topsoil (0–7.5 cm) samples (mean of 0.75 mg kg⁻¹) was about 7 times greater than the forest background concentration of Cd in the Waikato region (0.11 mg kg⁻¹), and also greater than the background Cd concentration in NZ pastoral soils (0.43 mg kg⁻¹), and the NZ national average soil baseline (0.16 mg kg⁻¹, sampling depth 10 cm) (Taylor et al., 2007). However, the total concentration of Cd in our study was approximately the same as the Waikato region topsols (mean of 0.74 mg kg⁻¹) (sampled from 2007 to 2013) (Stafford et al., 2014). The mean concentration of Cd in topsols (0–7.5 cm) of Gley Soils (0.78 mg kg⁻¹, Te Kowhai) was greater than the mean concentration of Cd in topsols (0–7.5 cm) of NZ-wide pastoral soils (0.42 mg kg⁻¹ for Gley Soils) (Roberts et al., 1994). However, the concentration of Cd in allophanic topsols (0.77 mg kg⁻¹ for Horotiu, 0.83 mg kg⁻¹ for Bruntwood) was similar to that reported over 20 years ago (0.70 mg kg⁻¹ for Allophanic Soils in NZ pastures) (Roberts et al., 1994). The concentration of Cd in surface soils was 7–8 times greater than subsurface soil samples, indicating that added Cd was being absorbed and retained in the topsoil.

Our main finding showed that there were no significant differences in concentrations of Cd, or total mass of Cd, among the three soils investigated, which supports the inference that the variable charge of allophanic clays had little bearing on the overall accumulation patterns observed. Therefore our results contradict previous study results, which reported that Cd sorption to Allophanic Soils was greater than non-Allophanic Soils (Bolan et al., 2013; Stafford et al., 2015) and confirm the results of Zanders (1998) that at the farm scale, Soil Order is not a determinant of Cd distribution. However, across New Zealand, at a landscape scale there are some differences between the Cd contents in different Soil Orders which reflect differences in land use and thus fertilizer history among different Soil Orders (Gray et al., 1999; Longhurst et al., 2004; McDowell et al., 2013).

There were no differences in Cd fractionation (determined by sequential extraction) in topsoil, indicating that there was little to differentiate the topsoils across the soil series. The lack of significant differences in Cd concentration among different soils, supports use of the Tiered Fertilizer Management System (TFMS) with one management system for these soil types.

Cd sorption increases with higher soil pH (Naidu et al., 1994; Gray et al., 1999). The pH values recorded in this study varied between 5.1 and 6.5 in the three soils with no significant differences between soil samples. We can conclude that pH was probably not important for controlling Cd adsorption capacity in the topsoils sampled. This is noteworthy given that Fe and Mn oxhydroxides minerals in these soils were identified by the sequential extraction as the primary phases controlling Cd accumulation, because pH values between 5 and 6.5 coincide with the adsorption edge for hydrous ferric oxides (Stumm, 1992).

Variable charge components of Allophanic Soils (allophane) should have modulated Cd sorption to a large degree between pH values of 5 and 7 (Parfitt, 1990). The fact that we did not observe differences in Cd accumulation between series therefore implies that the pH conditions in these soils did not drive substantial differences in the CEC between soil types, possibly because sorption was influenced by organic surface coatings on the mineral assemblages encountered (Gray et al., 1999). This is more plausible, given that the dominant type of allophane in New Zealand is the Al-rich allophane (Al:Si ≈ 2.0) (Parfitt, 1990; Holmgren et al., 1993) with a point of zero charge of more than pH 6 (Harsh, 2011; Yuan and Wada, 2012). It is probable that the allophane surfaces in the studied soils developed a net positive-to-neutral charge, as they have mostly pH of <6. Under these conditions it might be expected that the allophane clays present in the Horotiu and Bruntwood soils would only weakly retain Cd. Hence, it is likely that other phases in Allophanic Soils (i.e., metal oxides and organic matter) were mainly responsible for the observed retention of Cd in the uppermost layer of topsoil. We may predict that as increasing proportions of surface binding sites in soil minerals and organic matter become occupied by Cd, and other fertilizer-derived cations, then the proportion of Cd capable
of being mobilized will increase. Similarly, changes in Cd mobility may occur due to changes in soil pH or following amendments, such as additions of compost (Hanc et al., 2009).

The Zn/Cd ratio increased with soil depth and the Zn/Cd ratio in topsoils was lower than the NZ native soils and NZ pastures, which supports the inference that phosphate fertilizer application was responsible for Cd accumulation in topsoils (Loganathan et al., 1995; Zanders et al., 1999). The U/Cd ratio increased with depth in all soil types and the U/Cd ratio in the Bruntwood soil was higher than in the Horotiu or Te Kowhai soils, possibly indicating that relative to Cd, U was more mobile in the Bruntwood than Horotiu or Te Kowhai soils. The increase of U/P and Cd/P ratios with depth in both Bruntwood and Te Kowhai soils in comparison to the constant pattern in the Horotiu soil, suggests that the U and Cd were more mobile than P in the Te Kowhai and non-allophanic part of the Bruntwood soil, whereas in the Allophanic Soil materials, P, Cd and U appear to have been equally mobile.

There were significant-to-moderate correlations between P, Zn, Cu, Mn and Cd in the soils studied. Cu, Zn, Mn and Cd can also be derived from superfertilizer phosphates (David et al., 1978; During, 1984; McLaughlin and Singh, 1999; Bolan et al., 2003; Reiser et al., 2014); therefore the correlation of P with Cu, Zn and Mn was to be expected. The significant correlation between Zn and Cd was unsurprising, given the strong similarity in the chemistry of Cd and Zn (Kross et al., 1995). The correlations between P, Cd and U (Fig. 5, Table 4) suggest that Cd and U are derived mainly from phosphate fertilizers. Cu and Zn are probably also additionally enriched from some other anthropogenic sources such as animal health remedies and supplements (Anderson et al., 2012) which are widely used in the Waikato region and thus contribute Zn and Cu to soil (Taylor et al., 2010).

5. Conclusions

There were no significant differences in the concentration and total mass of Cd among the three contrasting soils with the same fertilizer history. Thus Cd concentration was more dependent on the amount of fertilizer applied than the soil characteristics. The Cd fractionation in the three different topsoils was similar. Therefore our data support use of the same Tiered Fertilizer Management System approach (which introduces different management requirements based on the concentration of Cd in the soil) for all these soils. Whether other Soil Orders also accumulate Cd to the same degree requires further exploration.

The Zn/Cd ratio increased with soil depth and was lower than the Zn/Cd ratio in unfertilized NZ topsoils, indicating that more Cd than Zn has been accumulated in farmed soils. The U/Cd, U/P and Cd/P ratios highlighted the possibility that U was more mobile than Cd, and both U and Cd were more mobile than P in the Te Kowhai and Bruntwood soils.

Cd, U and P were enriched in topsoils with minimal movement to the subsoil. Cluster analysis suggested a common source, most likely phosphate fertilizer. The correlation between Cu and Zn may reflect a common source, most likely animal health remedies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.geodres.2016.05.001. These data include Google maps of the most important areas described in this article.

References

Chapter 4. Isotope tracing of long-term cadmium fluxes in an agricultural soil

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Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil

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Supporting Information

ABSTRACT: Globally widespread phosphate fertilizer applications have resulted in long-term increases in the concentration of cadmium (Cd) in soils. The accumulation of this biotoxic, and bioaccumulative metal presents problems for the management of soil-plant-animal systems, because the magnitude and direction of removal fluxes (e.g., crop uptake, leaching) have been difficult to estimate. Here, Cd isotopic compositions (δ114/110Cd) of archived fertilizer and soil samples from a 66 year-long agricultural field trial in Winchmore, New Zealand, were used to constrain the Cd soil mass balance between 1959 and 2015 AD, informing future soil Cd accumulation trajectories. The isotopic partitioning of soil Cd sources in this system was aided by a change in phosphate source rocks in 1998 AD, and a corresponding shift in fertilizer isotope composition. The dominant influence of mixing between isotopically distinct Cd end-members was confirmed by a Bayesian modeling approach. Furthermore, isotope mass balance modeling revealed that Cd removal processes most likely increased in magnitude substantially between 2000 and 2015 AD, implying an increase in Cd bioaccumulation and/or leaching over that interval. Natural-abundance stable isotopes are introduced here as a powerful tool for tracing the fate of Cd in agricultural soils, and potentially the wider environment.

INTRODUCTION

Cadmium (Cd) is a harmful metal that has accumulated in agricultural soils, mainly as a result of phosphate fertilizer applications.1−5 Cadmium is a natural contaminant in phosphate source rocks6 which persists in fertilizers and can accumulate in soils, plants and higher organisms. In 1997 AD, responding to concerns over Cd accumulation in agricultural soils, the New Zealand (NZ) fertilizer industry changed the main source of phosphate fertilizers from Nauru (guano-derived) phosphorite (about 450 mg Cd kg−1 P) to a mixture of new sources including Moroccan source rocks, with the effect of lowering Cd concentrations in fertilizers. Since 1997 AD, fertilizers produced in NZ have had no more than 280 mg Cd kg−1 P.7,8

Research on long-term Cd accumulation trends in soils benefits from field trials run over several decades with continuity of land-management practice. A recent study addressing Cd concentration in soils from the long-term Winchmore field trial in New Zealand showed that the rate of Cd accumulation started to reach a plateau in the period since ~2000 AD.9 This indicated that post 2000 AD, Cd inputs in fertilizers were lower than outputs from the soil zone (leaching, plant uptake). However, the extent to which the soil Cd burden (after 2000 AD) was from historical or recent fertilizer applications remained in question.

Stable isotope ratio analysis is a powerful tool for the source identification of environmental contaminants, assuming that end-members are isotopically distinct and isotope fractionations are small and/or well constrained. This approach is increasingly being applied to the study of the origin, and environmental history of heavy metals and other anthropogenic contaminants,10,11 including in atmospheric aerosols,12,13 water,14−16 sediment17−20 and soil14,21−26 and even materials as diverse as meteorites and lunar soil.27,28 Cadmium stable isotopes are being more routinely applied to the study of cadmium’s environmental mobility and fate,29 and can also inform the biogeochemistry of the soil–plant system including plant-uptake of Cd,11 which has been shown to fractionate Cd between soil and wheat, with preferential accumulation of lighter isotopes over heavier isotopes in roots relative to grain.

Difficulties in the management of Cd accumulation in agricultural soils are currently compounded by uncertainty over

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the sources of Cd, since routine Cd monitoring is a comparatively recent phenomenon. It is also difficult to evaluate the effect that management strategies have on the accumulation of Cd and delineate whether changes in the total Cd pool reflect historical, or more recent Cd additions. Therefore, the objective of this research was to evaluate the utility of Cd stable isotope ratios as a tracer of Cd sources in soil samples from the long-term Winchmore field trial, where annual superphosphate (a manufactured P fertilizer) applications began in ca. 1949 and have continued to the present day. Based on the Cd isotopic composition of the control site subsoil (approximating native soil–Cd), topsoil samples from the Winchmore archive, as well as historical and recent fertilizers, we calculated the changing proportion of Cd in Winchmore topsoil through time using a Bayesian mixing model. This approach was extended using an isotope-enabled Cd mass balance to evaluate the influence of fertilizer inputs and removal mechanisms on Cd accumulation through time.

### MATERIALS AND METHODS

**Study site.** Soil samples were taken from the Winchmore research farm on the Canterbury Plains of the South Island, New Zealand (43° 47 S, 171° 48 E, 167 m above sea level, annual rainfall 740 mm/yr). The soil at Winchmore is Lismore Stony Silt loam (Orthic Brown [New Zealand], Udic Ustochrept [USDA]) which is developed from moderately weathered greywacke loess. The selected physical and chemical characteristics of the soil including pH, organic carbon, nitrogen and soil texture were reported by Condron and Goč. The soil is developed on outwash plains formed by the weathering of the Southern Alps, which are dominantly composed of greywacke sandstone gravels, stratigraphically defined as Paleosole. Two different trials were conducted at Winchmore: long-term fertilizer and long-term irrigation trials that were established in 1952 and 1949, respectively. For the irrigation trial, 250 kg ha⁻¹ of superphosphate was applied annually, but irrigation was applied at different soil moisture trigger values (dryland treatment with no irrigation, 10% moisture and 20% moisture). Soil samples were selected from the top 7.5 cm of the irrigation trial (dryland treatment; plot 15) from 1959, 1961, 1967, 1974, 1979, 1993, 1999, 2002 (Waikato University Archive), 2004, and 2009 (courtesy of Richard McDowell, AgResearch), and an additional sample was collected in 2015. One control plot soil sample from unfertilized (native) soil was taken from the subsurface layer (25–30 cm depth) of an adjacent paddock which has the same geology and was expected to have a similar chemical composition to the topsoils (before fertilization). Phosphate rock and fertilizer samples were obtained from Ballance Agri-Nutrients Ltd. (Tauranga, New Zealand), including samples from Nauru and Christmas Island (main sources of phosphorite for phosphate fertilizer manufacture prior to 1997 AD), fertilizer from the mid-1980s, and archived fertilizers from 1998, 2000, 2001, 2005, 2007, 2009, 2011, 2013, and 2015 (all used in the Winchmore trials) were also analyzed. Isotopic analyses were performed on two independently chemically processed aliquots of each sample of soil, phosphorite or fertilizer, with the exception of fertilizers from 1998, 2001, 2005, 2011, and 2013, for which just one sample was analyzed for isotopic composition.

**Cadmium Concentration and Isotopic Composition Analysis of Soils and Fertilizers.** All samples were dried and sieved (<2 mm) and then digested using a method described in Salzmanzadeh et al. with some minor modifications: The reagents were pipetted out of the polypropylene tube without any filtration and transferred to clean polypropylene tubes for ICP-MS analysis at the University of Waikato. The samples were not filtered in order to avoid any introduction of Cd from filter papers. To avoid any contamination, sample preparation was carried out in a class-100 laminar flow hood. Also, all sample tubes and vials were thoroughly acid-washed in clean reagent grade HCl at room temperature, then in 50% quartz distilled HCl (overnight). Finally all lab-ware was rinsed thoroughly (5 times with Milli-Q deionized water). All acids were purified in a Savillex DST-1000 acid purification system to parts-per-trillion (ppt)-grade (Cd blank <100 ppt). Cadmium concentration was determined by using a quadrupole ICP-MS (PerkinElmer Elan, Waltham, MA) at University of Waikato, New Zealand following calibration using NIST-traceable standards (Inorganic Ventures, Christiansburg, VA, USA).

After measuring the concentration of Cd, aliquots of each sample digest, corresponding to approximately 50 ng of Cd, were transferred to University of Otago, New Zealand for isotopic analysis following a double-spike method (full methods provided in Supporting Information (SI) Methods 1, Table S1).

Cadmium isotopic composition is generally expressed as the deviation of $^{114}$Cd/$^{110}$Cd ratio of a sample with respect to the $^{114}$Cd/$^{110}$Cd composition of a standard in parts-per-thousand ($\delta^{114}$Cd/$^{110}$Cd) (eq 1). In this study, Cd isotopic composition was measured by multiple-collector ICP-MS (MC-ICPMS) using a Nu Plasma HR instrument (Nu Instruments Ltd., U.K.) and methods modified from previous protocols. A DSN 100 desolubing nebulizer fitted with a 100 μL/min perfluoroalkoxy (PFA) nebulizer was used as the sample introduction system. The NIST 3108 Cd isotope standard sourced from the National Institute of Science and Technology (NIST), U.S., was used as the “zero delta” normalizing standard. Repeat measurements of the NIST 3108 standard give rise to an external reproducibility of 0.04 δ that is comparable to the 2 SE internal precision associated with individual measurements (SI Figure S1). Using these protocols, standard reference materials give values that are identical, within error, to certified values.

$$\delta^{114}/110\text{Cd} = \left(\frac{^{114}\text{Cd} / ^{110}\text{Cd}}{^{114}\text{Cd} / ^{110}\text{Cd}}\right)_{\text{sample}} - 1 \times 1000$$  

All Cd concentrations reported in this study were determined by isotope dilution using eq 2:

$$[\text{Cd}]_{\text{sample}} = \left(\frac{^{114}\text{Cd} / ^{110}\text{Cd}}{^{114}\text{Cd} / ^{110}\text{Cd}}\right)_{\text{mixture}} - \left(\frac{^{114}\text{Cd} / ^{110}\text{Cd}}{^{114}\text{Cd} / ^{110}\text{Cd}}\right)_{\text{spike}} \times \frac{\text{mass of sample}}{\text{mass of spike}} \times \frac{\text{fraction of } ^{114}\text{Cd in the sample}}{\text{fraction of } ^{114}\text{Cd in the spike mixture}}$$

where $^{114}\text{Cd} / ^{110}\text{Cd}_{\text{mixture}}$, $^{114}\text{Cd} / ^{110}\text{Cd}_{\text{sample}}$, and $^{114}\text{Cd} / ^{110}\text{Cd}_{\text{spike}}$ are the $^{114}\text{Cd} / ^{110}\text{Cd}$ ratios of the spike-sample mixture, sample and double spike, respectively, after correction for the instrumental mass bias, while $[^{111}\text{Cd}]_{\text{spike}}$ is the concentration of $^{111}\text{Cd}$ in the double spike and $[\text{Cd}]_{\text{sample}}$ is the Cd concentration of the sample.

**Sequential Extraction Method.** In an attempt to constrain the Cd speciation in the Winchmore soil system, the topsoil collected in 2015 (two replicates) was sequentially extracted with 1 M HCl, 0.1 M HCl, 0.1 M HNO₃, 0.1 M NaOH, and 0.1 M NH₄OAc. In each extraction procedure, the soil sample (1 g) was mixed with 40 mL of the specified reagent and allowed to sit for 40 min, followed by agitation on a Vortex mixer for 2 min. The supernatant was then separated from the soil by centrifugation at 4000 rpm for 10 min. The concentrations of Cd in each supernatant were measured using the same protocol as above. The results were reported as percentage of total Cd in the sample.
extracted following the method of Sun et al.39 (full method provided in SI Methods 2, Table S2).

**Bayesian Mixing Model.** Stable isotope data combined with a Bayesian modeling approach have been used before to estimate the contribution of multiple sources of elements in environmental samples.15,40,41 However, this is the first time this approach has been used for the Cd stable isotope system. We used an open source linear isotopic mixing Bayesian modeling strategy devised by Arendt, Aciego and Hetland14 to estimate the fractional contribution of different sources of Cd through time. Matlab 2013 was used with code introduced by Arendt, Aciego and Hetland14 with some modifications: Arendt, Aciego and Hetland14 defined the code based on the isotope ratios of two different elements (for example δ18O and δD), but we instead defined the model based on the isotope ratio of a single element (δ114/110Cd). The original Matlab code was configured for three different sources, but we defined only two sources for pre-2000 soils and three sources for post-2000 soils.

**pH Adsorption Edge Experiment.** pH is the most important variable controlling the adsorption of metals to soil surfaces.42 Therefore, a pH adsorption edge experiment was carried out to determine the pH-dependency of Cd adsorption on Winchmore topsoil. This experiment followed the method by Lee et al.43 (full method provided in SI Methods 3, Figure S3). Ideally, this can inform the potential of Cd to adsorb to soil under varying solution pH.

**Cadmium Balance (CadBal) Model.** A cadmium mass balance model (CadBal) has been available since 2005 in New Zealand, to estimate the potential accumulation of Cd in NZ soils.7,9 This model estimates the accumulation of Cd based on input data including the initial Cd concentration, farm and soil type, soil dry bulk density, fertilizer application rate, leaching, erosion, and atmospheric accession. We used this model to estimate the future concentration (up to 2030 AD) of Cd in topsoil and to compare our results with those of McDowell9 who studied the same site and reported a trend toward stabilizing Cd concentrations in the period after 2000 AD. CadBal was used to estimate the concentration of Cd through time based on four scenarios and using two sets of input data (Table 1, SI Table S4).

**Isotope Mass Balance Using CadBal Output.** An isotope mass balance approach was taken to constrain the importance of fertilizer inputs to topsoils relative to losses via cropping (i.e., grass growth and grazing) and leaching to groundwater. The input and output terms in this mass balance were constrained using CadBal (see previous section and I Methods 4) which generates loss terms for these vectors. CadBal is able to generate loss terms for erosion and input terms for atmospheric deposition, but these were neglected because of their very low magnitude (see SI Table S4). The resulting mass balance equation is given below (eq 3).

\[
[Cd]_{n+1,soil} \times \delta_{n+1,soil} = ([Cd]_{n,soil} + \delta_{n,soil})_{soil} + ([Cd]_{input} + \delta_{input})_{inputs} - ([Cd]_{input} \times \delta_{input} + [Cd]_{leach} \times \delta_{leach})_{outputs}
\]

\[
\delta_{n} is the isotope ratio of the compartment in per mil, and [Cd]_{n} is Cd concentration and derived as follows (eq 4):
\]

\[
[Cd]_{n+1} = [Cd]_{n} + (C_{input} ha^{-1} - C_{output} ha^{-1})_{n}/(bulk \ density \times depth \ ha^{-1})
\]

Isotope fractionation in each input and output term is calculated by multiplying the δ value (e.g., \( \delta_{n,leach} \)) by an appropriate α value (e.g., \( \alpha_{soil-leach} \)), where α defines the equilibrium partitioning of Cd isotopes between the reactant and product (eq 5).

\[
\delta_{n} + 1000 = (\delta_{n,leach} + 1000) \times \alpha_{n,b}
\]

This modeling utilized α values taken from Wiggenhauser et al.11 which were selected on the basis of relevance (i.e., similarity to soil properties). However, the available literature on Cd isotope fractionation factors do not currently cover soil- and grass- and water partitioning. Because of this deficiency we have approximated these terms using data from soil-wheat systems and extractable soil solutions (Ca(NO₃)₂),11 respectively.

### RESULTS AND DISCUSSION

**Cd Composition of Soils, Fertilizers and Source Rocks.** The Cd concentration and Cd isotopic composition of soils, fertilizers and phosphate rocks are presented in Table 1. Where data are available for two independently processed aliquots of the same sample (i.e., true replicate measurements of the soil), both Cd concentration and Cd isotopic composition are reported as the mean of the two replicate analyses with the two standard error of the mean values, calculated using the method of Conway et al.44 Corresponding data for each individual analysis is given in the SI (see Table S3). Otherwise, data is

<table>
<thead>
<tr>
<th>sample</th>
<th>Cd (mg kg⁻¹) ± SE</th>
<th>δ¹⁰⁶/¹²⁶Cd ± 2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>native (unfertilized) subsoil</td>
<td>0.02 ± 0.01</td>
<td>−0.33 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1959</td>
<td>0.16 ± 0.04</td>
<td>0.27 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1961</td>
<td>0.32 ± 0.00</td>
<td>0.10 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1967</td>
<td>0.24 ± 0.00</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1974</td>
<td>0.23 ± 0.00</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1979</td>
<td>0.25 ± 0.00</td>
<td>0.23 ± 0.05</td>
</tr>
<tr>
<td>topsoil 1986</td>
<td>0.29 ± 0.00</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>topsoil 1993</td>
<td>0.40 ± 0.00</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>topsoil 1999</td>
<td>0.35 ± 0.00</td>
<td>0.15 ± 0.04</td>
</tr>
<tr>
<td>topsoil 2002</td>
<td>0.35 ± 0.00</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>topsoil 2004</td>
<td>0.29 ± 0.00</td>
<td>0.09 ± 0.05</td>
</tr>
<tr>
<td>topsoil 2009</td>
<td>0.29 ± 0.00</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>topsoil 2015</td>
<td>0.30 ± 0.00</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>fertilizer 1980s</td>
<td>31.8 ± 0.04</td>
<td>0.25 ± 0.04</td>
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<tr>
<td>fertilizer 1998</td>
<td>26.4 ± 0.05</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>fertilizer 2000</td>
<td>27.0 ± 0.04</td>
<td>0.18 ± 0.04</td>
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<tr>
<td>fertilizer 2001</td>
<td>14.6 ± 0.05</td>
<td>0.01 ± 0.05</td>
</tr>
<tr>
<td>fertilizer 2005</td>
<td>21.0 ± 0.05</td>
<td>−0.11 ± 0.05</td>
</tr>
<tr>
<td>fertilizer 2007</td>
<td>23.3 ± 0.05</td>
<td>−0.11 ± 0.04</td>
</tr>
<tr>
<td>fertilizer 2011</td>
<td>15.4 ± 0.05</td>
<td>−0.11 ± 0.06</td>
</tr>
<tr>
<td>fertilizer 2013</td>
<td>20.6 ± 0.05</td>
<td>−0.12 ± 0.05</td>
</tr>
<tr>
<td>fertilizer 2015</td>
<td>8.27 ± 0.05</td>
<td>−0.17 ± 0.03</td>
</tr>
<tr>
<td>nauru phosphorite</td>
<td>96.4 ± 0.04</td>
<td>0.22 ± 0.04</td>
</tr>
<tr>
<td>Christmas Island phosphorite</td>
<td>38.0 ± 0.04</td>
<td></td>
</tr>
</tbody>
</table>

*Instrumental uncertainties are ±0.9% (2 SE).
reported as the mean value and 2 SE uncertainty for a single analysis, as per standard analytical protocols.

The concentrations of Cd in Nauru and Christmas Island rocks (Table 1) were in the range of previously reported concentrations (86–100 mg kg⁻¹ for Nauru and 31–56 mg kg⁻¹ for Christmas Island phosphate) (3,8,45). Cadmium concentrations in Winchmore plot-15 topsoils increased across the period 1959–2000 AD from ca. 0.16 to 0.35 mg kg⁻¹ (Figure 1a), replicating the change in concentration reported across the whole site by McDowell.9 The Cd isotope ratios of fertilized soils over the period 1959–2000 AD and the hatched rectangle shows the 2 SE range of isotope ratios from P fertilizer sources (Figure 1b), representing the mean concentration and Cd isotope ratio had been substantially modified from the natural situation (approximated by our control (Table 1)). Depleted δ¹¹⁴/¹¹⁰Cd values, presumably characteristic of the original (unfertilized) topsoil, were not observed in the earliest samples from our time series (1959 AD) which were taken a full nine years after the onset of fertilizer application, by which time we argue Cd concentrations and isotope ratios had been shifted substantially. Overall, the Cd isotope ratios of all fertilized soil samples were closest to the Cd isotopic compositions of pre-2000 AD fertilizers (Figure 1), suggesting that pre-2000 AD fertilizers strongly dominated the Cd budget in the Winchmore soils even after 2000 AD. However, this assessment does not account for potential fractionation effects in either fertilizers or soil samples, and this needs to be evaluated before sources can be attributed based on Cd isotope data.

**Cadmium Isotope Fractionation in Soil and Fertilizer Samples.** To produce a single superphosphate fertilizer (as used at Winchmore throughout the entire trial), finely ground phosphate rocks, largely consisting of fluorapatite (Ca₅(PO₄)₃F), are reacted with sulfuric acid and during this process all of the Cd originally present in the phosphate rock is retained within the fertilizer.54–56 Due to the high volatility and low boiling point (765 °C) of Cd,²⁹,₄⁸,₅₃, large (~0.6% level) isotope fractionations of Cd can occur during high-temperature industrial processes such as smelting and combustion.54–₅₆ However, Cd isotopic fractionation characteristics of the aforementioned high-temperature industrial processes, do not appear to occur during phosphate fertilizer manufacture which is carried out under low thermal conditions. This is borne out by a comparison between the δ¹¹⁴/¹¹⁰Cd of pre-2000 AD fertilizers and their Nauru and Christmas Island source rocks (Table 1; Figure 1). The data assembled here indicates that phosphate fertilizers retain an δ¹¹⁴/¹¹⁰Cd composition consistent with the guano-derived phosphorites of Nauru and Christmas Island.57 This indicates that either no Cd isotopic fractionation occurs during industrial processing, or that all Cd is quantitatively transferred from the phosphate source rock to the superphosphate fertilizer so that no net isotopic fractionation of Cd is observed.

A large degree of Cd isotopic fractionation in soil samples can occur due to biogeochemical processes in soils,¹¹ therefore the potential for in situ fractionation processes must be considered before mixing models can be used for source identification. Processes within agricultural soils that could cause Cd isotope fractionation include 1. Redox processes: elements usually occurring with one oxidation state (such as Cd) in natural systems tend to exhibit smaller isotopic variations in comparison to other metals with multiple oxidation states.¹⁰ However, Cd has a strong affinity for sulfides, forming in the presence of free H₂S under euxinic (anoxic and sulphidic, rather than anoxic, suboxic or oxic) conditions, so Cd is strongly redox-sensitive in this sense and
potentially fractionates during CdS formation. This is unlikely to be an issue in the free-draining soils of Canterbury, where sulfate reduction is inhibited by atmospheric gas exchange. 

2. Adsorption processes: reactions with organic matter and soil mineral surfaces have potential to induce Cd isotopic fractionation.\(^{10}\) Simulations of Cd isotopic fractionation in hydrothermal fluids between Cd species (cadmium hydroxide, cadmium nitrates, cadmium hydrates, cadmium chloride, and cadmium hydrosulfides) do not support a strong role for Cd speciation,\(^{54,58}\) although adsorption of Cd to synthetic birnessite (Mn oxyhydroxide) has been shown to cause a small fractionation effect at low ionic strength.\(^{59,60}\) Biological cycling: plant uptake has been shown to cause Cd isotope fractionation\(^{11}\) with diffusion and adsorption being largely responsible for Cd fractionation at the root-solution interface.\(^{10,61}\) In addition, permil-level Cd isotopic fractionation (by adsorption of lighter isotopes) has been observed during Cd uptake by phytoplankton (unicellular plants in the sunlit surface ocean).\(^{36,41,62,63}\) Natural weathering processes can also lead to Cd isotopic fractionation.\(^{64}\)

The enriched Cd isotopic composition of fertilized soils compared to the native soil show that there was some potential that the Cd isotope ratios in fertilized soils could have been fractionated due to biogeochemical or weathering processes in the soil zone.\(^{11,65,66}\) The fractionation of Cd isotopes within the fertilized soil samples during biological assimilation (i.e., by in situ bacterial communities, uptake by plant roots, or translocation in infiltrating soil water) is assessed in the section on Cd mass balance modeling (Mass Balance Modeling of Cd).

**Source Identification of Cd.** The following analysis takes a simple mixing approach and neglects potential fractionation effects, which are expected to be damped by the significant input signal of fertilizer-derived Cd. This latter point is addressed by mass balance modeling in a later section Mass Balance Modeling of Cd). Large changes in the \(\delta^{114/110}\text{Cd}\) of superphosphate are expected to have imparted changes in residual soil isotope values of a magnitude proportional to the fractional accumulation of Cd (based on the analysis of fertilizers (Table 1)).

Cadmium isotopic differences between end-members can be readily delineated using a \(\delta^{114/110}\text{Cd}\) versus \(1/\text{Cd}\) mixing diagram (Figure 2a).\(^{26,28,69}\) Soils did not align along a single line (Figure 2a) which indicates that Cd in fertilized soil samples originated from at least three different sources (i.e., native soil, pre-2000 AD fertilizer and post-2000 AD fertilizer), and also may have been affected by in situ processes.\(^{29}\) The \(\delta^{114/110}\text{Cd}\) of control soil did not follow a trendline with the fertilized soil samples, and was well isolated from the soils in terms of both Cd concentration and Cd isotope ratio (Figure 2a).

**Bayesian Attribution of Soil Cd Sources.** Based on the clear difference between the Cd isotopic end-members identified in this study, a binary mixing model was applied for pre-2000 AD soil samples, and a three-source mixing model was applied for post-2000 AD soil samples (Table 2). Different strategies were considered in selecting the end-members to calculate the fractional contribution of different sources through time (Table 2). Given the relatively small sample size in our set \((N = 26)\) we acknowledge that our approach is constrained and would be enhanced by additional replicate measurements. However, the Bayesian approach followed provides the best means of estimating the accompanying errors.
Table 2. Different End-Members Considered for Calculation of the Fractional Contribution of Cd Sources through Time in Topsoil Samples

<table>
<thead>
<tr>
<th>soil</th>
<th>endmember-1</th>
<th>endmember-2 (pre-2000 fertilizer)</th>
<th>endmember-3 (post-2000 fertilizer)</th>
</tr>
</thead>
</table>

(Figure 2a). However, because the pre- and post-2000 AD fertilizers were closer in composition than the native soil, this contributed to greater uncertainty in the model. Despite this source of uncertainty, the Bayesian mixing model demonstrates that Cd in the topsoil samples predominantly corresponds to inputs from Nauru-derived (pre-2000 AD) fertilizers. This is particularly clear in the 2015 AD analysis. We can conclude that Cd derived from Nauru continues to predominate in the soil up to the present day.

The mixing model outputs (Figure 2b) show from 2000 AD toward the present, fertilizer δ\(^{114}/^{110}\)Cd became increasingly isotopically distinct from the Nauru-derived fertilizers, thus increasing the confidence of the estimation of source contributions in the mixing model (Figure 2b). The estimate from 2015 AD shows that residual Cd in the Winchmore soil to the present day is dominated by historical fertilizer inputs. Hence, variability in the estimated fractional contribution between 2000 and 2015 AD can be rationalized as a possible statistical artifact arising from the close similarity of end-member δ\(^{114}/^{110}\)Cd values through this period. According to the mixing model the time-averaged fractional contribution of each source was about 10% for native soil, about 80% for pre-2000 AD fertilizers and about 17% for post-2000 AD fertilizers (Figure 2b). The results are therefore consistent with Cd in Winchmore soil samples being primarily derived from Nauru fertilizers, which is consistent with previous studies that have shown the typically long residence times of Cd in soil (e.g., up to 3000 years).\(^{66,76}\)

**What Caused the Recent Plateau in Winchmore soil Cd?** McDowell\(^{9}\) documented the recent decline in soil Cd accumulation at Winchmore. This study has extended McDowell’s analysis and has confirmed that Cd concentration in the topsoil has indeed plateaued. Furthermore, Cd isotopic analysis identifies pre-2000 AD fertilizers as the predominant source of Cd in the system. One possible conclusion based on this observation is that recent applications of Cd are not tending to accumulate. It is possible that this newer Cd is unable to effectively compete for adsorption sites in the soil matrix, thereby displacing the older Nauru-derived Cd. An alternative hypothesis is that in situ fractionation of Cd isotopes by pasture growth and/or leaching are modifying the observed isotope compositions (Figure 1b).

The analysis of sequential topsoil extracts confirmed that only a relatively small proportion (37%) of the total Cd was readily exchangeable (displacement by Mg\(^{2+}\) at pH 7) (SI Figure S2). Therefore, excluding hydrological changes associated with climate over the period, we identify two probable drivers of the concentration plateau:

- Reduced Cd inputs associated with the industry Cd management strategy
- Increases in the loss of Cd from the soil zone

As McDowell\(^{7}\) has documented, pH in the soil from the fertilizer trial at Winchmore changed throughout the series, with shifts between pH ∼ 6.0 and ∼ 5.6 over the period of soil Cd stabilization (1990–2015 AD). In order to evaluate the possible impact of soil pH changes, a Cd pH adsorption edge experiment was completed. This showed that the pH dependency of Cd adsorption is likely to be most strongly modulated between pH values of 3.5 and 5.3 (SI Figure S3). The pH of the control site subsoil in 2015 AD was determined at pH 5.4 and plot 15 topsoil from the same year had a pH of 5.2. The Cd adsorption efficiency of soil through time was estimated based on linear regression (R\(^2\) = 0.96) between %Cd adsorbed and pH in the adsorption edge experiment between pH values of 5.3 and 8 (SI Figure S3). The estimated Cd adsorption efficiency change corresponded to a shift of slightly greater than 2% (between pH 5.4 and 6.0). Over the same interval (1990–2015 AD), the Cd concentrations in plot 15 topsoil (this study) declined by ∼25%. This is therefore inconsistent with a pH control on Cd adsorption capacity. In order to better understand the mechanisms of Cd accumulation and loss at Winchmore, a mass balance modeling approach was taken.

**Mass Balance Modeling of Cd.** McDowell\(^{9}\) showed that reduced loading of Cd from fertilizer is sufficient to explain the observed Cd accumulation trends at Winchmore assuming lower total Cd in superphosphate fertilizer applications. Our analysis of fertilizer samples from the period 1998–2015 (Table 1) demonstrates that fertilizer Cd was actually higher (204.0 ± 66.8 mg Cd kg\(^{-1}\) P; n = 8) during this period than that assumed by McDowell previously\(^{9}\) (140 ± 60.62 mg Cd kg\(^{-1}\) P; n = 3). This difference in total concentration resulted in a large overprediction of soil Cd accumulation during the period post-2000 AD based on our better-constrained input data (Figure 3a).

The results of Cd mass balance modeling completed in this study and in McDowell\(^{9}\) demonstrate that the fertilizer Cd concentration data of McDowell best represented the period of early Cd accumulation between 1949 and 1998, whereas the detailed determinations of fertilizer Cd between 1998 and 2015 AD in this study provide improved constraint on Cd accumulation trends post-2000 AD (Figure 3a; see SI Table S4 for details of modeling scenarios). The second scenario (blue curve (Figure 3a)) overestimated Cd accumulation over the entire record because only two fertilizer samples for the period pre-2000 AD were considered (just one fertilizer sample for period of 1949–1998), whereas McDowell\(^{7}\) used five pre-2000 AD fertilizers. The third scenario (red curve (Figure 3a)) combined McDowell’s pre-1998 AD fertilizer concentration data (isotope ratio from our pre-1998 AD samples) and the post-1998 AD fertilizers characterized in this study. This third modeling scenario provides an improved fit to topsoil concentrations and isotope ratios through the period 1959–2000 AD (Figure 3a,b). However, important discrepancies were observed between the modeled and measured data after 2000 AD. Most importantly, the third scenario model output
overpredicted the concentration of Cd in topsoil in the most recent period (Figure 3a). This overestimation was tested in a fourth scenario, in which the leaching rate was doubled for the post-2000 AD period. The results of scenario four (SI Table S4) showed a closer correspondence to the measured Plot 15 Cd concentrations, post-2000 AD (red dashed line (Figure 3a)). The doubling of Cd removal by leaching did not substantially alter the modeled soil isotope ratios between the third (red line (Figure 3b)) and fourth scenarios (red dashed line (Figure 3b)).

The mass balance modeling results confirm that recent applications of P fertilizer have not resulted in an accumulation of Cd consistent with the model boundary conditions (for crop uptake/leaching (SI Table S4)) which gave good agreement for the period prior to 2000 AD (Figure 3a). This implies that removal of Cd by either leaching or crop uptake has increased during this most recent period. The modeled Cd isotope data appear to be consistent with this interpretation (Figure 3b). Slightly more enriched values of Cd isotopes in plot 15 soil (than predicted by scenario 4) may therefore indicate that

1. In situ processes acting on Cd may have fractionated the residual Cd pool toward heavier values than predicted by the Cd fractionation factors used here (Wiggenhauser et al.11); or
2. Cd from recent fertilizer applications contributed less to the total soil Cd isotope composition than predicted by the model (which assumes perfect mixing).

The modeled isotope ratios given in Figure 3b-c extend to 2030 AD and provide the means to systematically test the process of Cd accumulation and loss at this site. It would be beneficial to extend the analysis of Cd isotopes in the future to include Cd accumulated by pasture and Cd leached to groundwater. The predicted trend in exchangeable Cd over time is shown in Figure 3c.

Environmental Significance. This study has shown that Cd isotope ratios in fertilized soils were distinguishable from the control soils and were comparable to the source rocks used in fertilizer manufacture. Cadmium isotopic analysis is therefore a promising tool to trace the fate of fertilizer-derived Cd in the environment beyond the soil zone, provided the influence of possible additional biogeochemical processes that can potentially modify the Cd isotope signals of the soils are well constrained, and that the Cd isotopic composition and Cd concentration of the native soil are well-known. If the declining trend observed at Winchmore is emblematic of Cd behavior in soil systems elsewhere, it follows that the Cd is migrating from the soil zone, either through uptake by plants and animals, or by translocation down the soil profile and via erosive losses. Cadmium isotopes may therefore offer the potential to trace this Cd and monitor its environmental impact, at least in areas where substantial Cd contamination from other activities is scarce.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00858.
Table S1−S4, Figure S1−S3, Supplementary Methods 1−4, Matlab code (PDF)

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The manuscript was written through contributions of all authors. M.S. completed all laboratory work (column chemistry, extractions etc.) and the Bayesian and isotope mass balance modeling. MC-ICP-MS analyses were conducted by E.G. and C.S. A.H. secured funding, sampled soils from Winchmore, cowrote the final text with M.S., and produced the final versions of the figures for publication. L.S. provided archived Winchmore soil samples. C.J. assisted with Matlab coding. All authors have given approval to the final version of the manuscript.
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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(37) Abouchami, W.; Galer, S. J. G.; Horner, T. J.; Rehkämper, M.; Wombacher, F.; Xue, Z. C.; Lambelet, M.; Gault-Ringold, M.; Stirling,


Chapter 5. The effect of irrigation on cadmium, uranium, and phosphorus contents in agricultural soils

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The effect of irrigation on cadmium, uranium, and phosphorus contents in agricultural soils

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ABSTRACT

Cadmium (Cd) is a toxic metal which has accumulated in New Zealand agricultural soils due to phosphate fertilizer application. Understanding the contribution of plant uptake or leaching of Cd to observed Cd losses from soil is important. The concentration and distribution of Cd in irrigated and unirrigated soils with the same phosphate fertilizer history were investigated. Twenty-two pairs of soil samples from four depths (0–0.1, 0.1–0.2, 0.2–0.3 and 0.3–0.4 m) were taken from irrigated and unirrigated areas in the same field on dairy farms in three regions of New Zealand. The mean concentration of Cd at depths of 0–0.1 m and 0.1–0.2 m, as well as the cumulative masses of Cd (0–0.2, 0–0.3 and 0–0.4 m) in unirrigated soils were significantly higher (P < 0.05) than in irrigated soils. The concentration of phosphorus (P) at all depths (except for 0.2–0.3 m), as well as the cumulative mass of P in all depths of unirrigated soils, was also significantly higher (P < 0.05) than irrigated soils. However, no significant difference was detected in the concentrations of uranium (U) between irrigated and unirrigated soils. Irrigation induced a ∼7% Cd loss from topsoil (0–0.1 m), with the average rate of Cd loss from the top 0.1 m (due to irrigation) being 2.3 g ha⁻¹ yr⁻¹. This study therefore confirms that irrigation can enhance Cd mobilization, however Cd is mainly adsorbed to the surface soil.

1. Introduction

Cadmium (Cd) has accumulated in New Zealand (NZ) soils mainly from phosphate fertilizers (Loganathan et al., 2003; Schipper et al., 2011) which have been applied to NZ soils since the late 1800s. The dominant productive land use in New Zealand is grazed pasture which is generally accompanied by large amounts of phosphate fertilizer use (Parliamentary Commissioner for the Environment, 2004). There are concerns about the accumulation of Cd in soil because of its entry to the human food chain and potential adverse effects on health (Mortvedt, 1995). Cadmium has been described as being the trace metal of greatest concern with respect to food standards in New Zealand (Taylor et al., 2010). In order to understand the environmental fate of Cd, it is necessary to develop a full mass balance including fertilizer inputs as well as removal in products, erosion, and leaching through the profile.

The magnitude of Cd losses from soil via drainage are not well known with studies of Cd mobility in soils based largely on the mass balance approach. Many studies report minimal cadmium loss from soil. For instance, Loganathan and Hedley (1997) found that after 10 years of phosphate fertilizer application, less than 5% of applied Cd moved below 0.2 m and the uptake of Cd by plants ranged from 1.5 to 4.5% of total inputs. Similarly, Singh and Myhr (1997) were unable to detect downward movement of Cd through the profile of fertilized soils in Norway. Even in a loamy sand in South Carolina with a low cation exchange capacity (CEC), Cd movement below 0.15 m depth was negligible (< 3%) 30 months after the Cd application. Despite the low CEC in the aforementioned study, Fe and Al oxides were identified as the most important adsorbents of Cd in these soils (Martin and Kaplan, 1998). Cadmium appears to be even more immobilized in organic soils: in a lysimeter study of Cd losses from Organic soils, the leaching of Cd was not significant (less than 1% of added Cd from phosphate fertilizer application) over 12 months (Gray and McDowell, 2016).

While the aforementioned studies reported minimal loss of Cd by leaching, several other studies have found significant movement of Cd through the soil (Nicholson et al., 1996; Zanders et al., 1999a; Gray et al., 2003b). On an Australian sandy Podzol soil, about 50% of added Cd from fertilizer application over 20 years, had been lost from the top 0.075 m, with only 1–5% of soluble Cd taken up by plants. Some of the
added Cd had moved to a depth of at least 0.15 m (Williams and David, 1976). About 50% of added Cd had accumulated in the top 0.225 m of a NZ soil with less than 2% of Cd was taken by plants, implying that the remainder may have moved down through the soil profile (Rothbaum et al., 1986). McBride et al. (1997) also showed that 15 years after sewage sludge application, about 30% of Cd was removed from the topsoil of an orchard site in USA, which was attributed to possible leaching losses.

The majority of these previous studies were conducted on unirrigated lands and there is some evidence that increased water application through irrigation might increase Cd movement through topsoil due to increased infiltration (McLeod et al., 2015). The concentration of Cd in irrigated topsoils (0–0.075 m) of the Winchmore research farm in New Zealand (Lismore stony silt loam) was less than in non-irrigated topsoils (McDowell, 2012). Furthermore, at Winchmore, the concentration of Cd at depths of 0.075–0.15 and 0.15–0.30 m in irrigated soils was higher than in non-irrigated soils suggesting movement of Cd down the soil profile (McDowell, 2012). However, the Winchmore trial was flood irrigated and therefore may not be representative of the expanding area of pastures irrigated by overhead sprinklers in New Zealand (about 74% of NZ irrigated pastures are now being sprinkler irrigated) (Heller, 2008; Irrigation New Zealand, 2013). Reliable data on Cd losses from irrigated soils are currently lacking. Like Cd, uranium (U) is also a contaminant of phosphate fertilizers in NZ soils, and has been classified as “very toxic” (Health and Safety Executive, 1995) and is potentially mobile (Taylor and Kim, 2007). Uranium and phosphorus (P) have important roles in soils and U, Cd, and P are accumulating in agricultural soils from the same source (phosphate fertilizers).

The objective of this study was to determine the potential for loss of Cd, U, and P due to irrigation. We took advantage of the wide scale soil sampling campaign of adjacent irrigated, and unirrigated pastures, conducted by Mudge et al. (2016) that demonstrated losses of carbon and nitrogen stocks under irrigation. On each farm, both irrigated and unirrigated areas were sampled in the same field to ensure uniform fertilizer history and therefore Cd, U, and P inputs.

2. Materials and methods

2.1. Site and soil

Soil samples were taken from 22 paired irrigated and unirrigated pasture sites (grazed by dairy cattle) in three regions of New Zealand (Fig. 1). Ten cores (0.0254 m diameter) were taken from each irrigated and unirrigated area in the same field. On six of the 22 farms, two fields were sampled, and the two irrigated samples from the two fields were combined, as were the two unirrigated samples, giving one irrigated and one unirrigated sample. Samples from each group of 10 cores were combined for each of depths of 0–0.1, 0.1–0.2, 0.2–0.3 and 0.3–0.4 m and bulked into one composite sample for each depth. One site in the Canterbury region was sampled to only 0.3 m due to high stone content lower in the profile. The selection criteria considered when choosing sampling locations have been fully described by Mudge et al. (2016) along with further information on irrigation duration (ranging 3–20 years), soil orders, type of irrigation and long-term climate data (1972–2011) for each sampling site. The irrigated and unirrigated areas within a field were identified using local knowledge, Google Earth imagery, Irrigation Resource Consents and help from rural professionals (Mudge et al., 2016). Paired sites were selected based on the following criteria: 1. Irrigated and unirrigated areas were within 100 m of each other; 2. The irrigated areas had been irrigated for at least three years, while unirrigated areas had never been irrigated; 3. Soils and topography were the same between irrigated and unirrigated areas, and 4. Farm management (such as fertilizer application) was the same in irrigated and unirrigated areas (expect for irrigation) (Mudge et al., 2016).

2.2. Chemical analysis

Soil samples were digested following the method described in Mudge et al. (2016): the air dried (50°C) and sieved (< 2 mm) soil samples were digested using Aqua Regia (1 mL HNO₃ and 0.33 mL HCl) at 50°C. After centrifuging for 10 min at 4000 rpm and filtering at 0.45 μm, Cd, P, and U concentrations were determined using ICP-MS (Waltham, MA, USA) following calibration using NIST-traceable standards (Inorganic Ventures, Christiansburg, VA, USA). The detection limit of ICP-MS was 130 μg kg⁻¹ for P, 6.0 μg kg⁻¹ for Cd, and 0.02 μg kg⁻¹ for U.

The pH of soil samples was measured following Blakemore et al. (1987). Total carbon (C) of the soil samples was reported by Mudge et al. (2016).

2.3. Data analysis

The cumulative mass of elements in each depth was calculated using the element concentration, and soil dry bulk density calculated from the mass of oven dry soil for each depth and the sample volume (depth 0.1 m and diameter 0.0254 m).

The Minitab 17 software package and Wilcoxon signed rank test was used to test the significance of difference between the mean concentrations and cumulative mass of Cd, P, and U for all depths individually. The Wilcoxon signed rank test can be used to test the significance of differences when data are not normally distributed and was used to check the degree of significance in differences in Cd, P, and U concentrations and cumulative masses in the studied soils.

3. Results

3.1. Cadmium concentration and cumulative mass

The mean Cd concentration in unirrigated soil samples was higher (P < 0.05) than that for irrigated soils at depths of 0–0.1 m and 0.1–0.2 m (Table 1). The cumulative mass of Cd for depths of 0–0.2, 0–0.3 and 0–0.4 m in unirrigated soils was higher (P < 0.05) than in irrigated soils (Table 1).

There were no significant differences in soil dry bulk density between irrigated and unirrigated areas at the 0–0.4 m depth (with the mean of 1.15 T m⁻³ in unirrigated and 1.14 T m⁻³ in irrigated areas) as well as individual depths. However, soil dry bulk density at the 0–0.1 m depth in irrigated areas was marginally higher (P = 0.05) than in unirrigated areas, which may be the reason for the significant difference in Cd concentration for the top 0.1 m but not for total mass in the same depth (Table 1).

The number of years of irrigation may be expected to impact on the mobility of Cd, however, there was no significant relationship (R² = 0.13, P < 0.05) between irrigation duration and the amount of Cd loss from 0 to 0.4 m in irrigated soils (Fig. 2).

The estimation of losses of fertilizer-derived Cd from surface soils is not straightforward because the Cd content of fertilizers and the amount and type of fertilizers used at each site through time is not well documented. As we did not have detailed information about the fertilizer history of the sampling locations, we could not directly calculate the loss of anthropogenically added Cd in phosphate fertilizers. However, it was possible to calculate the amount and percentage of Cd loss due to irrigation using the difference in the total mass of Cd in irrigated and unirrigated soils divided by the number of years of irrigation (3–20 years) (Table 2). To assess whether the calculated loss of Cd due to irrigation was greater than the measurement error standard deviation of Cd determinations on paired soil samples was calculated. This standard deviation used different aliquots of the primary soil samples (independently digested by Aqua Regia and analysed by ICP-MS). This gave a final standard deviation of 0.003 mg kg⁻¹ between replicated measurements of five paired soil samples. While this measure
correctly represents the measurement error for the digestion and Cd analysis process, it is possible that an additional error due to sampling could have increased this value. This was controlled for however, by combining 10 soil samples at the time of sampling, from which a homogenised primary soil sample was generated.

The average loss of Cd due to irrigation was 2.3 g ha\(^{-1}\) yr\(^{-1}\) from the top 0.1 m and 7.2 g ha\(^{-1}\) yr\(^{-1}\) for 0–0.4 m (Table 2). The results of the total mass calculation showed that the maximum amount of Cd loss from the topsoil (0–0.1 m), due to irrigation, was about 7% and about 10% from the 0–0.4 m depth (Table 2).

The mean loss of Cd as well as the percentage of Cd removal from the 0–0.1 m depth was highest in the Bay of Plenty region (Pumice Soil) (Table 2). However, the mean loss and percentage of Cd removal from the 0–0.4 m depth was highest in the Canterbury region (Pallic, Recent, Gley, and Brown Soils) (Table 2).

### Table 1

Concentration and cumulative mass of Cd for different soil depths (\(P\) values < 0.05 are bolded, numbers in the brackets are standard errors).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Number of paired samples</th>
<th>Mean concentration of Cd (mg kg(^{-1}))</th>
<th>Depth (m)</th>
<th>Cumulative mass of Cd (kg ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unirrigated</td>
<td>Irrigated</td>
<td>(P)</td>
</tr>
<tr>
<td>0–0.1</td>
<td>22</td>
<td>0.33 (0.04)</td>
<td>0.29 (0.03)</td>
<td><strong>0.023</strong></td>
</tr>
<tr>
<td>0.1–0.2</td>
<td>22</td>
<td>0.22 (0.03)</td>
<td>0.19 (0.02)</td>
<td><strong>0.009</strong></td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>22</td>
<td>0.10 (0.01)</td>
<td>0.09 (0.01)</td>
<td>0.516</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>21</td>
<td>0.06 (0.01)</td>
<td>0.04 (0.01)</td>
<td>0.187</td>
</tr>
</tbody>
</table>

Fig. 1. Sampling locations of irrigated and unirrigated soils.
3.2. Phosphorus and uranium concentration and cumulative mass

The concentration of P in the 0–0.1, 0.1–0.2 and 0.3–0.4 m depth intervals, as well as the cumulative mass of P in all depths in unirrigated soils, were significantly higher (P < 0.05) than in irrigated soils (Table 3). In contrast, there were no significant differences between the concentrations of U in irrigated and unirrigated soils. However, as for Cd, the cumulative mass of U in depths of 0–0.2, 0–0.3 and 0.4–0.4 m of unirrigated soils was significantly higher (P < 0.05) than irrigated soils (Table 4).

There was a moderate relationship between the cumulative loss of Cd and the cumulative loss of P from the 0–0.4 m depth (R² = 0.25, P < 0.05), however there was no significant relationship between the cumulative loss of Cd and U.

3.3. Soil pH and carbon content

Overall, the mean soil pH was 5.6 (range 4.8–7.0) for unirrigated and 5.7 (range 4.9–6.5) for irrigated soil samples, and there were no significant differences in pH for either irrigated or unirrigated soil samples at any depth. The mean carbon content decreased down the soil profile and the mean carbon content in all four depths of irrigated soils was significantly lower (P < 0.05) than the unirrigated soil samples (full data presented in Mudge et al., 2016). There was no significant relationship between the loss of Cd and the difference between the pH in irrigated and unirrigated areas from each individual depth. There was a moderate relationship between the carbon content and Cd concentration in topsoil (0–0.1 m) samples (R² = 0.41, P < 0.05). The cumulative loss of Cd and cumulative loss of C from 0 to 0.4 m were also moderately correlated (R² = 0.33, P < 0.05).

4. Discussion

4.1. Cadmium, phosphorus and uranium concentration and total mass

In comparison with previous studies of irrigation effects on Cd movement at individual sites, our analysis encompassed a broad range of soils and irrigation regimes. We measured a lower concentration of Cd in irrigated soil compared to unirrigated soil (0–0.1 and 0.1–0.2 m), which had a mean of 0.04 mg kg⁻¹ less Cd (depth of 0–0.1 m). Our results were consistent with findings at the flood-irrigated Winchmore site where there was a difference of about 0.07 mg kg⁻¹ in the top 0–0.075 m (McDowell, 2012). Because of 0.04 mg kg⁻¹ of average difference between irrigated and unirrigated soils (depth of 0–0.1 m) which was 13 times greater than the standard deviation (0.003 mg kg⁻¹), the calculated losses of Cd were greater than the associated measurement error. The concentration of Cd in the soils sampled (mean of 0.31 mg kg⁻¹ in the top 0.1 m of soils in our study) were relatively low in comparison to the mean concentration of Cd in topsoils of NZ dairy farms (mean of 0.58 mg kg⁻¹) and overall in NZ pastures (0.44 mg kg⁻¹) (Cavanagh, 2014). However, the higher mean concentration of Cd in NZ dairy farms is due to the high concentration of Cd in the Waikato (0.74 mg kg⁻¹) and Taranaki (0.71 mg kg⁻¹) regions, which skew the mean concentration of Cd in NZ pastures and dairy farms. A threshold value for Cd in NZ soils of 1.8 mg kg⁻¹ has been identified. If soils reach the threshold value then no further phosphate fertilizers should be applied without a site-specific investigation and risk assessment (MAF, 2011).

The lower concentration of Cd in the 0–0.1 m depth in irrigated areas than unirrigated areas was consistent with the results of McDowell (2012) who reported higher Cd concentrations in the topsoil (0–0.075 m) of unirrigated soils in comparison to irrigated soils. However, in the McDowell (2012) study, the irrigated subsoils (0.075–0.15 and 0.15–0.30 m) contained more Cd than unirrigated subsoils (McDowell, 2012). McDowell (2012) reported a gradual decrease in soil pH at the sampled Winchmore research farm since the mid-1970s, and postulated this decrease in pH increased Cd mobility and movement deeper into the soil or uptake by plants. Also, the use of flood irrigation at Winchmore may have enhanced the leaching of Cd (Gray et al., 1999a).

The greatest difference in Cd concentration between the irrigated and unirrigated topsoil (0–0.1 m) in our study was in the Pumice Soil (0.40 mg kg⁻¹), which may be due to the generally sandy nature and therefore greater potential for drainage in the Pumice Soil (Gray et al., 2003a). The annual average of Cd loss from each soil order from the 0–0.4 m depth was highest for Pallic Soil (20.0 g ha⁻¹ yr⁻¹) followed by Pumice (7.4 g ha⁻¹ yr⁻¹), Brown (2.4 g ha⁻¹ yr⁻¹), Gley (0.5 g ha⁻¹ yr⁻¹) and Recent (0.1 g ha⁻¹ yr⁻¹) soils (Table 2). The higher reported Cd loss in Pallic Soil was due to one sample with a Cd loss of 55 g ha⁻¹ yr⁻¹ (Table 2) which skewed the mean of Cd loss from Pallic Soil. Pumice Soil (sandy nature) showed the second highest loss of Cd.

In comparison to Cd, the magnitude of the difference between P concentration and cumulative mass in irrigated and unirrigated soils was higher. The ‘more significant’ result for P than Cd may have been due to irrigation increasing downward movement of P more than Cd (Condron et al., 2006), or greater plant uptake and translocation of P than Cd. The greater plant uptake was supported by Mackay et al. (1987) and Loganathan and Hedley (1997) who showed that at a fertilized site, the plant recovery of P (17–19%) was greater than Cd (1.5–4.5%).

There was no significant difference between the concentrations of U in irrigated and unirrigated soils. Therefore, in comparison to Cd, U mobility was less influenced by irrigation, which was also concluded by McDowell (2010). The strong adsorption and minimal leaching of U was also observed by Taylor (2007), who showed that almost all
applied U in P fertilizers had been retained in the soil with minimal leaching. Taylor (1997) also concluded that less than 1% of added U in soil was available for plant uptake or leaching. Rothbaum et al. (1979) and Heshmati-Rafsanjani (2009) also showed greater leaching and plant uptake of P than U.

Because we used the same method for sampling in irrigated and unirrigated areas and due to no systematic difference in bulk density, or the variability of bulk density between irrigated and unirrigated areas, the probability that sampling or measurement error contributed to the significant differences observed between irrigated and unirrigated areas is low. Indeed if sampling or measurement error was high, the probability of detecting significant differences would be lower. While there was only significant difference at depths of 0–0.1 and 0.1–0.2 m between concentration of Cd in irrigated and unirrigated areas, Cd

<table>
<thead>
<tr>
<th>Region</th>
<th>Soil order</th>
<th>Irrigation duration (years)</th>
<th>Total mass of Cd in 0–0.1 m (kg ha⁻¹)</th>
<th>Cumulative mass of Cd in 0–0.4 m (kg ha⁻¹)</th>
<th>Total Cd removed (%) from 0 to 0.1 m</th>
<th>Total Cd removed (%) from 0 to 0.4 m</th>
<th>Total Cd removed (% from 0 to 0.1 m)</th>
<th>Total Cd removed (% from 0 to 0.4 m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bay of Plenty</td>
<td>Un Pumice</td>
<td>20</td>
<td>0.50</td>
<td>1.17</td>
<td>(½/72) × 100 = 10%</td>
<td>(½/72) × 100 = 15%</td>
<td>(½/72) × 100 = 2.5</td>
<td>(½/72) × 100 = 8.5</td>
</tr>
<tr>
<td>(BoP) Un Pumice</td>
<td>Irr</td>
<td>12</td>
<td>0.45</td>
<td>1.00</td>
<td>5.9%</td>
<td>9.2%</td>
<td>1.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Un Pumice</td>
<td>12</td>
<td>0.32</td>
<td>0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un Pumice</td>
<td>13</td>
<td>0.28</td>
<td>0.43</td>
<td>−3.4%</td>
<td>22%</td>
<td>20</td>
<td>−0.7</td>
<td>−8.6</td>
</tr>
<tr>
<td>Un Pumice</td>
<td>14</td>
<td>0.29</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un Pumice</td>
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<td>0.44</td>
<td>0.91</td>
<td>14%</td>
<td>22%</td>
<td>5.0</td>
<td>16.7</td>
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<td>0.71</td>
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<tr>
<td>BoP (mean)</td>
<td>Un Pumice</td>
<td>0.44</td>
<td>0.81</td>
<td>11%</td>
<td>9.0%</td>
<td>4.8</td>
<td>7.4</td>
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</tr>
<tr>
<td>Irr</td>
<td>0.37</td>
<td>0.71</td>
<td></td>
<td></td>
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<tr>
<td>Un Brown</td>
<td>14</td>
<td>0.32</td>
<td>0.70</td>
<td>28%</td>
<td>17%</td>
<td>6.4</td>
<td>8.6</td>
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</tr>
<tr>
<td>Un Brown</td>
<td>13</td>
<td>0.19</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Un Brown</td>
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<td>0.78</td>
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<td>5.1%</td>
<td>1.7</td>
<td>3.3</td>
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<td>0.74</td>
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<tr>
<td>Manawatu-Wanganui (MW)</td>
<td>Un Brown</td>
<td>20</td>
<td>0.29</td>
<td>0.62</td>
<td>−28%</td>
<td>−19%</td>
<td>−8.0</td>
<td>−12</td>
</tr>
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<td>0.74</td>
<td></td>
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<tr>
<td>Un Recent</td>
<td>12.5</td>
<td>0.22</td>
<td>0.47</td>
<td>18%</td>
<td>−3.8%</td>
<td>2.4</td>
<td>−0.8</td>
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<tr>
<td>Un Recent</td>
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<td>0.25</td>
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<td>Gley</td>
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<td>0.26</td>
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<tr>
<td>MW (mean)</td>
<td>Un Brown</td>
<td>0.25</td>
<td>0.58</td>
<td>4.2%</td>
<td>5.9%</td>
<td>1.0</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Irr</td>
<td>0.23</td>
<td>0.37</td>
<td></td>
<td></td>
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<td>Un Pallic</td>
<td>20</td>
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<td>0.85</td>
<td>25%</td>
<td>42%</td>
<td>4.0</td>
<td>18</td>
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</tr>
<tr>
<td>Irr</td>
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<td>0.84</td>
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<tr>
<td>Un Brown</td>
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<td>0.18</td>
<td>0.64</td>
<td>5.6%</td>
<td>17%</td>
<td>0.7</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Irr</td>
<td>15</td>
<td>0.17</td>
<td>0.53</td>
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<td>Un Pallic</td>
<td>8</td>
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<td>1.26</td>
<td>20%</td>
<td>35%</td>
<td>8.8</td>
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<tr>
<td>Irr</td>
<td>12</td>
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<td>0.69</td>
<td>8.7%</td>
<td>16%</td>
<td>1.7</td>
<td>9.2</td>
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<tr>
<td>Un Gley</td>
<td>12</td>
<td>0.21</td>
<td>0.58</td>
<td></td>
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<tr>
<td>Irr</td>
<td>3</td>
<td>0.21</td>
<td>0.61</td>
<td></td>
<td></td>
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<td>Pallic</td>
<td>10</td>
<td>0.16</td>
<td>0.47</td>
<td>13%</td>
<td>0.0%</td>
<td>2.0</td>
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<tr>
<td>Pallic</td>
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<td>0.61</td>
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</tr>
<tr>
<td>Canterbury</td>
<td>Un Pallic</td>
<td>20</td>
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<td>0.76</td>
<td>5.7%</td>
<td>13%</td>
<td>1.0</td>
<td>9.8</td>
</tr>
<tr>
<td>Irr</td>
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<td>0.64</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mean of all</td>
<td>Un Pallic</td>
<td>0.25</td>
<td>0.76</td>
<td>7.0%</td>
<td>9.9%</td>
<td>2.3</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Irr</td>
<td>0.23</td>
<td>0.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a New Zealand soil classification (Hewitt, 1998) and Keys to soil taxonomy (Soil Survey staff, 2014).
b Difference between mass of Cd in irrigated and unirrigated areas divided by mass of Cd in unirrigated area.
c Difference between mass of Cd in irrigated and unirrigated areas divided by number of years of irrigation.
d Unirrigated.
e Irrigated.
concentrations were lower for all depth increments. This consistency of differences would have contributed to the cumulative mass differences being significant, which also would be the case for the significant difference between the cumulative mass of U in irrigated and unirrigated areas while there was no significant difference observed for U concentration.

4.2. Soil pH and carbon content

Soil pH was approximately constant down the profile, as previously reported by McIntosh et al. (1997) and Gray et al. (2003a), with no significant differences between irrigated and unirrigated soils as was also reported by Condon et al. (2006). Although soils with lower C contents and lower pH might be expected to exhibit more Cd mobility (Gray et al., 1999a; McLaren et al., 2005), this was not observed here (due to moderate correlation between loss of Cd and loss of C and no significant correlation between the loss of Cd and the difference between the pH in irrigated and unirrigated areas) nor by Zanders et al. (1999b) or Gray et al. (2003a). Therefore, from our results none of the other measured soil properties (soil texture, C, pH) appeared to singly exert strong control on the mobility of Cd in soil. Cd mobility is expected to be a function of pH, cation exchange capacity (CEC), Fe and Mn oxides, soil texture, organic carbon concentration, and the origin of anthropogenic Cd (Kim and Ferguson, 1992; Gray et al., 1999b, 2003b).

4.3. Cadmium loss calculation

The annual rate of Cd removal in irrigated areas in comparison to unirrigated areas (2.3 g ha⁻¹ from depth of 0–0.1 m and 5.5 g ha⁻¹ from depth of 0–0.2 m) was greater than the reported amount of Cd leached in previous studies. For example, 1–2 g ha⁻¹ yr⁻¹ (top 0.2 m, Cd loss determined from soil Cd concentration) (Tjell and Christensen, 1992); 0.27–0.86 g ha⁻¹ yr⁻¹ (top 0.25 m, Cd loss determined from measuring leachate) (Gray et al., 2003a) and 2.4–4.9 g ha⁻¹ yr⁻¹ (top 0.225 m, Cd loss determined from measuring leachate) (Nicholson et al., 1996), and within the range of leaching reported in other studies: 2.4 g ha⁻¹ yr⁻¹ (top 0.075 m, Cd loss determined from soil Cd concentration) (McDowell, 2012), 4.6–7.7 g ha⁻¹ yr⁻¹ (depth of 0 cm to top of E horizon, Cd loss determined from soil Cd concentration) (Zanders et al., 1999a). The range of variations could be attributed to the soil type, soil properties, and type of experiment (the measurement of Cd concentration in leachate or Cd concentration measurement in soil profile).

The 7% loss of Cd from the 0–0.1 m depth (Table 2) only represents the Cd loss due to irrigation and the total amount of lost Cd (including Cd in parent material) may well be greater due to losses associated with rainfall, and/or plant and animal uptake that occur in both irrigated and unirrigated parts of pastures. Plant uptake of Cd in irrigated soils has also been shown to be greater than unirrigated soils (McDowell, 2012; Abraham et al., 2016), but plant uptake of Cd is generally less than Cd leaching (Zanders et al., 1999a). For example, Rothbaum et al. (1986) showed that about 2% of Cd added to grass-clover pastures in New Zealand was taken up by plants, while about 50% of added Cd was lost from the top 0.225 m. Net Cd uptake by grazing animals is generally considered negligible, with more than 99% of Cd ingested by animals excreted (Van Bruwaene et al., 1984; Lee et al., 1994, 1996). Irrigation can also lead to higher rates of transpiration, which may also contribute in increasing Cd accumulation by plants (Legind et al., 2012). Thus, we hypothesize that Cd losses in our study were due to enhanced leaching and/or plant and animal uptake due to the extra water addition from irrigation.

The estimated 7% loss of Cd from the top 0.1 m and about 10% of Cd loss from 0 to 0.4 m (Table 2) supported the results of previous studies that measured losses of about 5–15% (depth of 0–0.25 m, natural or simulated rain) (Gray et al., 2003a) of added Cd due to leaching. Similarly, losses associated with leaching and plant and animal removal ranged from 10% (depth of 0–0.12 m, non-irrigated) (Loganathan and Hedley, 1997) and 6% (depth of 0–0.075 m, non-irrigated) (Williams and David, 1976). Therefore, our results from a range of soils and regions showed that although Cd was relatively immobile in soils, and the majority of applied Cd was adsorbed to the topsoil, irrigation can increase the loss of Cd.

5. Conclusions

The mean concentration of Cd in surface soil (0–0.1 and 0.1–0.2 m) and cumulative mass to 0.4 m of unirrigated soils was significantly higher (P < 0.05) than the irrigated soils. The concentration of P (all depths except for 0.2–0.3 m) and the cumulative mass of P (all depths) in unirrigated soils was significantly greater (P < 0.05) than the irrigated soils. However, there was no significant difference between the concentration of U in irrigated and unirrigated soils. The significant difference in P and Cd concentration and nonsignificant difference in U concentration between irrigated and unirrigated soils, implies that irrigation probably had more effect on P, and less effect on U, losses relative to Cd. The average rate of Cd loss from the topsoil (0–0.1 m) attributed to irrigation was 2.3 g ha⁻¹ yr⁻¹ and 7.2 g ha⁻¹ yr⁻¹ for

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Number of paired samples</th>
<th>Mean concentration of P (mg kg⁻¹)</th>
<th>Depth (m)</th>
<th>Cumulative mass of P (kg ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unirrigated</td>
<td>Irrigated</td>
<td>P</td>
<td>Unirrigated</td>
</tr>
<tr>
<td>0–0.1</td>
<td>22</td>
<td>803.0 (67)</td>
<td>712.0 (73)</td>
<td>0.014</td>
</tr>
<tr>
<td>0.1–0.2</td>
<td>22</td>
<td>498.0 (50)</td>
<td>411.9 (33)</td>
<td>0.014</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>22</td>
<td>298.1 (31)</td>
<td>247.0 (27)</td>
<td>0.091</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>21</td>
<td>244.4 (36)</td>
<td>189.3 (27)</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 3
Concentration and cumulative mass of P for different soil depths (P values < 0.05 are bolded, numbers in the brackets are standard errors).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Number of paired samples</th>
<th>Mean concentration of U (mg kg⁻¹)</th>
<th>Depth (m)</th>
<th>Cumulative mass of U (kg ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unirrigated</td>
<td>Irrigated</td>
<td>P</td>
<td>Unirrigated</td>
</tr>
<tr>
<td>0–0.1</td>
<td>22</td>
<td>0.88 (0.08)</td>
<td>0.82 (0.09)</td>
<td>0.119</td>
</tr>
<tr>
<td>0.1–0.2</td>
<td>22</td>
<td>0.70 (0.10)</td>
<td>0.66 (0.10)</td>
<td>0.069</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>22</td>
<td>0.53 (0.11)</td>
<td>0.51 (0.10)</td>
<td>0.091</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>21</td>
<td>0.49 (0.13)</td>
<td>0.49 (0.12)</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Table 4
Concentration and cumulative mass of U for different soil depths (P values < 0.05 are bolded, numbers in the brackets are standard errors).
0–0.4 m. We estimate that about 7% and 10% of Cd was lost from 0.1 m and 0.4 m depths, respectively. Therefore, it was concluded that Cd was generally immobile and preferably absorbs in the surface soil, and that Cd losses by irrigation are an important factor mitigating long-term Cd accumulation in agricultural soils.

Acknowledgements

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References


Heshmati-Rafsanjani, M., 2009. Comparative Studies on the Solubility of Uranium and


Chapter 6. Summary and conclusions

6.1 Introduction

This research was divided into three main parts. The objectives of this thesis were to:

1. Determine if the distribution of Cd varies between soils with contrasting mineralogy and drainage characteristics, but the same phosphate fertiliser history,
2. Evaluate the utility of Cd stable isotope ratios ($\delta^{114/110}\text{Cd}$) to trace the sources of Cd in NZ soils through time and distinguish the contribution of different sources of Cd in NZ soils, and,
3. Determine whether there is a difference in the concentration of Cd in irrigated and unirrigated soils within the same paddock (hence with the same phosphate fertiliser history).

Each research chapter (chapters 3-6) addressed one of the aforementioned research objectives. This chapter summarises the whole thesis, discusses the relationship between the three investigations that were completed, provides suggestions for further research, and gives an overall conclusion to the work.

6.2 Summary

6.2.1 Cadmium distribution in three contrasting soils

Research objective 1 was addressed in Chapter 3. The distribution of Cd in three soils with contrasting mineralogy and drainage characteristics, but the same fertiliser history, was compared. Within the Tiered Fertiliser Management
System (TFMS) (under which the NZ fertiliser industry manages Cd in soils), there is an implicit assumption that Cd behaves similarly in all soils. Thus the question arises, is it reasonable to apply one management regime to all soils? Within the Waikato region, three soils with contrasting drainage and mineralogy occur in a close spatial distances and can all be found within single paddocks where fertiliser and grazing management have been consistent. Thus an opportunity to test the fate of Cd in contrasting soils is afforded. Ten paddocks were selected from Scott Farm (175°22' E, 37°46' S, DairyNZ, Waikato, New Zealand) with a known fertiliser history (of at least 10 years). Areas of well-drained Horotiu (Orthic Allophanic Soil), moderately-drained Bruntwood (Impeded Allophanic Soil) and poorly-drained Te Kowhai (Orthic Gley Soil) soils were identified within each paddock. Six horizons (0-60 cm) were sampled in each soil and the concentration of Cd was determined.

The key results were:

- The mean concentration of Cd in topsoil (0-7.5 cm) samples was 0.77 mg kg\(^{-1}\) (range 0.56-0.99) in the Horotiu soil, 0.83 mg kg\(^{-1}\) (range 0.60-1.11) in the Bruntwood soil and 0.78 mg kg\(^{-1}\) (range 0.46-0.96) in the Te Kowhai soil.
- There were no significant differences in the concentration or the total mass of Cd between the three soils.
- The mean concentration of Cd in all topsoil (0-7.5 cm) samples (mean of 0.75 mg kg\(^{-1}\)) was about 7 times greater than the forest background concentration of Cd in the Waikato region (0.11 mg kg\(^{-1}\)), therefore Cd was enriched in soil samples in comparison to the background concentration.
• Cadmium was mainly retained near the soil surface regardless of mineralogy and drainage status of the soils.

• The lack of difference in Cd distribution between contrasting soil series supports the use of one Cd management system tool (TFMS) for all of these soils.

• The fractionation pattern of Cd (bound to Fe-Mn oxides > exchangeable > bound to organic matter > bound to carbonates ~ residual) was similar in each of the three soils.

• The results of cluster analysis suggested a common source for Cd, U and P, most likely phosphate fertilisers.

6.2.2 Isotope evaluation of cadmium in agricultural soils

Since 1997, the main source of fertilisers in New Zealand has changed from Nauru Island rock phosphate to a variety of rock phosphates with lower concentrations of Cd. Since around 2000, the concentration of Cd in soil from a long-term irrigation and fertiliser trial at the Winchmore research farm (171° 48' E, 43° 47' S, Canterbury, NZ) has plateaued (McDowell 2012). The second research objective (addressed in Chapter 4) was to utilise the stable isotope ratios of Cd ($\delta^{114/110}$Cd) to trace the sources of Cd in NZ soils to check the cause of the plateau in Cd concentration and distinguish the contribution of different sources of Cd at the Winchmore research farm.

Two trials: a long-term fertiliser and long-term irrigation trial have been conducted at Winchmore (McDowell 2012). Twelve fertilised soil samples (0-7.5 cm) from 1959-2015 (irrigation trial, dryland treatment), one control (unfertilised natural background) subsoil sample (25-30 cm), nine fertiliser
samples from the 1980s to 2015 and two phosphate rock samples (Nauru and Christmas Island) were selected for the analysis. The concentration and isotope ratios of Cd (δ^{114/110}Cd) in all samples were determined. A pH adsorption edge experiment was conducted on unfertilised soil to check the potential of soil to adsorb Cd at various pH levels (3.5-8.5). Bayesian modelling was employed to calculate the fractional distribution of various sources of Cd (pre-2000 fertilisers, post-2000 fertilisers and native soil) through time. A Cd mass balance program (CadBal) was used to estimate the concentration of Cd up to 2030.

The key results were:

- The isotopic compositions of pre-2000 fertilisers (δ^{114/110}Cd = 0.10 ± 0.05 to 0.25 ± 0.04) were comparable to the Nauru source rocks (δ^{114/110}Cd = 0.22 ± 0.04) but distinct from the control subsoil (δ^{114/110}Cd = -0.33 ± 0.04) and post-2000 fertilisers (δ^{114/110}Cd range of -0.17 ± 0.03 to 0.01 ± 0.05). The isotopic compositions of fertilised soil samples ranged from δ^{114/110}Cd = 0.08 ± 0.03 to δ^{114/110}Cd = 0.27 ± 0.04, which were comparable to pre-2000 fertilisers. Thus, it becomes possible to distinguish the sources of Cd within the soil using this isotope technique.

- Three main sources were identified for Cd in soil samples; pre-2000 phosphate fertilisers, post-2000 phosphate fertilisers and the control (unfertilised natural background) soil.

- Bayesian modelling of isotopes confirmed the dominant contribution of pre-2000 fertilisers (~80%) in increasing the concentration of Cd in soils. According to this mixing model, the contribution of Cd in soil samples was about 17% for post-2000 fertilisers and about 10% for the native soil.
• Thus, although the main sources of phosphate fertilisers have changed since 1997, Cd in the Winchmore soil was predominantly from application of pre-2000 fertilisers.

• Based on the results of a pH adsorption edge experiment and the pH in soil samples, over the interval of 1990-2015, Cd adsorption efficiency of soil decreased with a shift of around 2%, but the concentration of Cd decreased by ~25% over the same interval. Therefore, the reduction in Cd concentration in the soils since around 2000 reflects the reduced Cd loadings from fertilisers and removal in product/leaching.

• The plateau/decline in the Cd concentration since 2000, following the reduction of Cd in fertilisers, reported by McDowell (2012) was confirmed.

• Results from the CadBal model confirmed that assuming no increase in the amount of Cd in fertilisers, the concentration of Cd at the Winchmore research farm (irrigation trial, dryland treatment) is expected to remain at the present level or decline through time.

6.2.3 The amount of cadmium in irrigated and unirrigated soils with the same fertiliser history

The third research objective, addressed in Chapter 5, was to determine the potential for Cd loss by comparing the concentration of Cd in irrigated and unirrigated soils within the same paddock.

Twenty-two pairs of soil samples (depths of 0-10, 10-20, 20-30 and 30-40 cm) were taken from irrigated and unirrigated areas of different dairy farms of three regions of New Zealand (Bay of Plenty, Manawatu-Wanganui, and Canterbury).
The paired soil samples were from the same paddock, so had the same fertiliser history.

The key results were:

- The mean concentration of Cd (depth of 0-10 cm and 10-20 cm) and the cumulative mass of Cd (depths of 0-20, 0-30, and 0-40 cm) were higher ($P < 0.05$) in unirrigated soils than in irrigated soils.
- Cumulative mass of Cd was about 7% less in the top 10 cm and about 10% less in the 0-40 cm depth in irrigated soil than unirrigated soil.
- The difference between irrigated and unirrigated soils could be due to increased Cd loss as a result of either increased plant uptake and/or movement down the soil profile in irrigated areas compared to unirrigated areas.
- The mean rate of Cd loss was about 2.3 g ha$^{-1}$ yr$^{-1}$ from the top 10 cm and about 7.2 g ha$^{-1}$ yr$^{-1}$ from the 0-40 cm depth interval.
- The “relative loss” of Cd was less than loss of P and more than loss of U, reflecting that, compared to Cd, U is more, and P is less, strongly adsorbed to soil.
- The results confirmed that Cd was generally immobile and prefers to adsorb to the near surface of the soils studied, however irrigation can probably enhance the mobility of Cd.

6.3 Discussion

The key conclusion of the comparison between contrasting soil types was that it was reasonable to use one standard approach to Cd management for all the three investigated soils as per the Tiered Fertiliser Management System (TFMS).
approach. The potential for leaching of Cd to the groundwater was not assessed in chapter 3; however, the results showed that the concentration of Cd at a depth of nearly 60 cm was very similar to the background concentration of Cd, which suggests that little Cd had moved down the soil profile.

For the same pH, the CEC in the Horotiu soil would be expected to exceed the CEC of the Te Kowhai soil, because the Horotiu soil contains more allophane, which has a variable charge (Bolan et al. 2003). As the pH of the soils investigated were similar, the concentration of Cd in the Horotiu soil could be expected to be greater than in the Te Kowhai soil, due to the higher CEC in Horotiu soil. However, no significant differences were observed in Cd accumulation between soil types, which implied that the pH conditions in these soils did not drive substantial differences in the CEC between soil types, possibly because sorption was influenced by organic surface coatings on the mineral assemblages encountered (Gray et al. 1999). This was plausible, given that the dominant type of allophane in NZ soil is the Al-rich allophane (Al:Si ≈ 2.0) (Parfitt 1990; Holmgren et al. 1993) with a point of zero charge of more than pH 6 (Harsh 2011; Yuan & Wada 2012).

It was probable that the allophane surfaces in the studied soils developed a net positive-to-neutral charge, as the pH of the soils was mostly less than 6 (mean of 5.8). Under these conditions, the allophanic clays present in the Horotiu and Bruntwood soils would possibly retain Cd weakly. Hence, according to the fractionation pattern of Cd in soils, metal oxides and organic matter in Allophanic soils were possibly responsible for the observed retention of Cd in the uppermost layer of topsoil.
Cluster analysis confirmed that Cd originated mainly from phosphate fertilisers, which has also been widely reported in previous studies (e.g. Gray et al. 1999; Loganathan et al. 2003). However, the contribution of different sources of Cd, including phosphate fertilisers, in increasing the amount of Cd as well as the fate of Cd in NZ agricultural soils were unknown. Furthermore, due to the change of the main source of phosphate fertilisers in New Zealand in 1997, answers to questions of how changing the main source of phosphate fertilisers has affected the Cd distribution in NZ soils, and what was happening to the historic Cd, were essential. Therefore, for the second part of this research, Cd isotopes were employed to trace the sources and fate of Cd and also the contribution of old (pre-2000) and new (post-2000) fertilisers in increasing the amount of Cd in NZ agricultural soils.

The key conclusion of the isotope analysis of soil, phosphorite and fertiliser samples was that, for the first time in New Zealand, we were able to distinguish various sources of Cd (unfertilised native soil, pre-2000 and post-2000 fertilisers) in soils from the Winchmore research farm, using isotope analysis. We adapted cadmium balance model (CadBal) and the mass balance approach was taken to constrain the future concentration and isotope ratios of Cd in the soil sampled. The fractionation factor of Cd within the fertilized soil samples, due to Cd uptake by plant roots and translocation in infiltrating soil water, was utilized from a recent study by Wiggenhauser et al., 2016.

The irrigated areas of Winchmore research farm soils showed a translocation of Cd from a depth of 0-7.5 cm to the deeper levels (7.5-15 and 15-30 cm) (McDowell 2012). However, there have been conflicting conclusions on the
mobility of Cd in NZ soils in previous studies (Loganathan & Hedley 1997; Martin & Kaplan 1998; Gray et al. 2003).

To assess the possible effect of irrigation on Cd mobility, the concentration of Cd was determined in soils from irrigated and unirrigated areas. The soil samples were from three different regions of New Zealand to obtain a wide range of soils from different climate regions. The key conclusion of the comparison between irrigated and unirrigated areas was that Cd is generally immobile and adsorbed to the near surface soil. However, there was a significant difference ($P < 0.05$) between the accumulative mass and concentration of Cd in irrigated and unirrigated areas, which did suggest that irrigation may have increased the mobility of Cd.

Therefore, our results from a wide range of soils and regions showed that although Cd was relatively immobile in soils, and the majority of applied Cd was adsorbed to the topsoil, that Cd losses due to irrigation are an important factor mitigating long term Cd accumulation in agricultural soils.

### 6.4 Suggestions for further research

Although several aspects have been covered in this project, there are still more questions about Cd in soils.

The horizontal distribution of Cd was compared in three soil types (from two Soil Orders) in Chapter 3. How other Soil Orders accumulate Cd, is a question that needs to be answered by further research. It is important to manage the application of phosphate fertilisers in New Zealand employing the Tiered Fertiliser Management System (TFMS) approach. The implicit assumption of the TFMS management approach is that all soils show similar rates of Cd accumulation.
Therefore, it would be beneficial to extend this research and check the behaviour of Cd in other Soil Orders.

Isotope analysis of Cd is a novel tool which has been employed in this research, for the first time in New Zealand, to trace the fate of Cd in agricultural soils. The declining/plateau trend of Cd accumulation in soils at the Winchmore research farm (long-term irrigation trial) showed that Cd was probably taken up by plants and subsequently removed in animal product, and/or moved down through the soil profile and possibly leaching to groundwater. Cadmium isotope analysis can therefore offer the potential to trace and monitor the Cd distribution in the wider environments including plants, animals and water bodies. Reduction in the amount of Cd in phosphate fertilisers led to a plateau or declining trend in Cd accumulation in fertilised soils. However, the results are from only one case study (Winchmore research farm) and the investigation of other NZ farms is required to make a comprehensive conclusion.

The comparison between irrigated and unirrigated areas showed that Cd was generally immobile, however, there have been some studies in New Zealand that have shown significant mobilisation of Cd in soils (Zanders et al. 1999; Gray et al. 2003). Therefore, a comprehensive study on Cd mobility in all Soil Orders would help the management of Cd in NZ soils.

### 6.5 Conclusions

Cadmium is a non-essential and potentially toxic heavy metal, which has accumulated in NZ soils as a result of phosphate fertiliser application. Because agriculture is one of the major drivers of the NZ economy, and there is concern
about potential adverse effect to human health from Cd in the food produced, research about the status of Cd in NZ soils is essential.

Comparison of Cd concentration and total mass in contrasting soils showed that there was no significant difference in the concentration and total mass of Cd between the three investigated soils. Cadmium was mainly retained in the near-surface in both well-drained and poorly-drained soils and both allophane and halloysite dominated clay mineralogy. Therefore, the use of the same Tiered Fertiliser Management System to manage soil Cd in the investigated soils is supported.

The isotopic composition approach helped trace the fate of Cd, and for the first time, Cd isotope ratios ($^{\delta^{114}}_{110}$Cd) was used to distinguish various sources and determine their fractional distributions. The dominant contribution of pre-2000 fertilisers in the accumulation of Cd in NZ soils (at Winchmore) was shown. Therefore, isotope analysis was shown to be a powerful tool, which can help manage the amount of Cd in NZ soils and possibly the wider environment, including water and higher organisms.

Comparison between irrigated and unirrigated soils showed a significant increase in Cd loss/mobility in irrigated areas. 10% Cd loss (depth of 0-40 cm) was reported in the irrigated areas in comparison to the unirrigated areas. The results showed that Cd was generally immobile and preferably adsorbed in topsoil and that possible Cd losses by irrigation were an important factor mitigating long-term Cd accumulation in agricultural soils.
References


Appendix A. Supplementary data and sampling location map for Chapter 3 (Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history)

Table S1. Soil samples location, depth, description and element concentrations (mg kg$^{-1}$)

<table>
<thead>
<tr>
<th>Farm Number</th>
<th>Sample Number</th>
<th>Sample Location</th>
<th>Sample Depth (cm)</th>
<th>Soil Type</th>
<th>Horizon</th>
<th>Soil Texture</th>
<th>Cd concentration (mg kg$^{-1}$)</th>
<th>P concentration (mg kg$^{-1}$)</th>
<th>U concentration (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C21</td>
<td>1</td>
<td>37°46'20.54&quot;S, 175°21'53.43&quot;E</td>
<td>0-7.5</td>
<td>Horotiu</td>
<td>Ap</td>
<td>Sandy Loam</td>
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<td>7.5-15</td>
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<td>Ap</td>
<td>Sandy Loam</td>
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<td>3</td>
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<td>Horotiu</td>
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<td>Sandy Loam</td>
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<td>827.42</td>
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<td>Bruntwood</td>
<td>Ap</td>
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<td>2.29</td>
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<td>Sample Depth (cm)</td>
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<td>Horizon</td>
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<td>P concentration (mg kg(^{-1}))</td>
<td>U concentration (mg kg(^{-1}))</td>
</tr>
<tr>
<td>-------------</td>
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<tr>
<td>C27</td>
<td>165</td>
<td>37°46'26.72&quot;S, 175°21'45.80&quot;E</td>
<td>15-30</td>
<td>Horotiu</td>
<td>B/A</td>
<td>Loamy Sand</td>
<td>0.33</td>
<td>539.95</td>
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<tr>
<td>C27</td>
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<td>37°46'26.72&quot;S, 175°21'45.80&quot;E</td>
<td>30-40</td>
<td>Horotiu</td>
<td>Bw</td>
<td>Loamy Silt</td>
<td>0.22</td>
<td>229.19</td>
<td>1.01</td>
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<td>40-50</td>
<td>Horotiu</td>
<td>Bw</td>
<td>Loamy Silt</td>
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<td>168</td>
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<td>Horotiu</td>
<td>Bw</td>
<td>Loamy Silt</td>
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<td>169</td>
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<td>Bruntwood</td>
<td>Ap</td>
<td>Loamy Silt</td>
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<td>1959.59</td>
<td>1.81</td>
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<tr>
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<td>170</td>
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<td>7.5-15</td>
<td>Bruntwood</td>
<td>Ap</td>
<td>Loamy Silt</td>
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<td>171</td>
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<td>Bruntwood</td>
<td>A/B</td>
<td>Loamy Silt</td>
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<td>Bruntwood</td>
<td>Bw</td>
<td>Loamy Silt</td>
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<td>Bruntwood</td>
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<td>Silty Clay</td>
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<td>16.11</td>
<td>0.81</td>
</tr>
<tr>
<td>C27</td>
<td>174</td>
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<td>45-60</td>
<td>Bruntwood</td>
<td>Bg</td>
<td>Silty Clay</td>
<td>0.02</td>
<td>7.56</td>
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<td>175</td>
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<td>0-7.5</td>
<td>Te Kowhai</td>
<td>Ap</td>
<td>Silt Loam</td>
<td>0.87</td>
<td>2314.85</td>
<td>1.83</td>
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<td>7.5-15</td>
<td>Te Kowhai</td>
<td>Ap</td>
<td>Silt Loam</td>
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<td>1273.97</td>
<td>1.56</td>
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<td>177</td>
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<td>15-23</td>
<td>Te Kowhai</td>
<td>Ap</td>
<td>Silt Loam</td>
<td>0.51</td>
<td>763.58</td>
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<td>Farm Number</td>
<td>Sample Number</td>
<td>Sample Location</td>
<td>Sample Depth (cm)</td>
<td>Soil Type</td>
<td>Horizon</td>
<td>Soil Texture</td>
<td>Cd concentration (mg kg⁻¹)</td>
<td>P concentration (mg kg⁻¹)</td>
<td>U concentration (mg kg⁻¹)</td>
</tr>
<tr>
<td>-------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>------------------</td>
<td>-----------</td>
<td>---------</td>
<td>--------------</td>
<td>---------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>C27</td>
<td>178</td>
<td>37°46'27.43&quot;S, 175°21'45.50&quot;E</td>
<td>23-35</td>
<td>Te Kowhai</td>
<td>B/A</td>
<td>Loamy Clay</td>
<td>0.22</td>
<td>224.15</td>
<td>0.62</td>
</tr>
<tr>
<td>C27</td>
<td>179</td>
<td>37°46'27.43&quot;S, 175°21'45.50&quot;E</td>
<td>35-45</td>
<td>Te Kowhai</td>
<td>B(g)</td>
<td>Silty Clay</td>
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<td>37.94</td>
<td>0.48</td>
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<tr>
<td>C27</td>
<td>180</td>
<td>37°46'27.43&quot;S, 175°21'45.50&quot;E</td>
<td>45-60</td>
<td>Te Kowhai</td>
<td>B(g)</td>
<td>Silty Clay</td>
<td>0.03</td>
<td>17.17</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Figure A1. Google earth screen shot of sampling location (Scott Farm)
Appendix B. Supporting Information for Chapter 4 (Isotope tracing of long-term cadmium fluxes in an agricultural soil)

Summary

Supplementary Methods 1 (sample preparation for Cd concentration and isotope analysis)

Table S1. Chemical separation procedure for pre-concentration and purification of Cd from soil, fertilizer and rock phosphate samples

Figure S1. Cadmium isotopic measurements of the NIST 3108 standard during a single analytical session. During this session, the average 2 SE uncertainty for individual measurements is ±0.049 δ and is comparable to the 2 SD external reproducibility (±0.044 δ) based on repeat measurements of this standard

Supplementary Methods 2 (Sequential extraction)

Table S2. Sequential extraction method procedure

Figure S2. The percentage of Cd in different fractions of topsoil 2015

Supplementary Methods 3 (pH adsorption edge experiment)

Figure S3. Adsorption of $1 \times 10^{-4}$ M Cd onto Winchmore soils

Table S3. Cd concentration and isotope compositions of Cd for all individual topsoil, fertilizer, phosphorite and control subsoil samples, where data are available for two independently processed replicate aliquots

Table S4. Input data for the CadBal model in our study and McDowell 3 for the dryland treatment of the Winchmore long-term irrigation trial

Supplementary Methods 4 (isotope mass balance)

Matlab code
Supplementary Methods 1 (sample preparation for Cd concentration and isotope analysis)

All samples were prepared for Cd isotopic analysis in the Centre for Trace Element Analysis, within the Department of Chemistry, University of Otago under Class 10 (ISO 4) laminar flow within a Class 100 (ISO 5) clean room. Ultra-high purity acids and deionized water (>18.2 MΩ) supplied by a Milli-Q Element purification system (Millipore, USA) were used for all reagent, equipment, and sample preparation. Teflon vials (Savillex, USA) were used throughout for the chemical preparation of samples. All sample processing equipment was rigorously acid cleaned before use following standard protocols. For each digest, a known amount of sample corresponding to ~50 ng Cd was transferred to a teflon vial for further processing. A $^{111}$Cd-$^{110}$Cd double spike, with a calibrated $^{110}$Cd/$^{111}$Cd ratio of 1.95193, was admixed to each sample before sample preparation to allow for reliable correction of instrumental mass bias and for any isotopic fractionation that occurred during chemical processing. Then, a two-stage ion exchange separation procedure was conducted using AG1-X8 and AG-MP1 to isolate and purify the Cd fraction from the remaining sample matrix (Table S1). Using this approach, the recovery of Cd was routinely >90 % and often exceeded 95%. The total procedural blank during chemical preparation is typically less than 7 pg of Cd, which is negligible for all samples analysed with respect to both Cd isotopic composition and concentration.
Table S1. Chemical separation procedure for pre-concentration and purification of Cd from soil, fertilizer and rock phosphate samples

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Volume (mL)</th>
<th>Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG1-X8 anion-exchange resin</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>2 M HNO₃ (resin cleaning)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>Mili-Q water (resin cleaning)</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>8 M HCl (conversion to Cl⁻ form, wash)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (resin conditioning, wash)</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (sample solution)</td>
<td>5.5</td>
<td>Matrix</td>
</tr>
<tr>
<td>0.7 M HCl</td>
<td>5.5</td>
<td>Matrix</td>
</tr>
<tr>
<td>1 M HCl</td>
<td>5.5</td>
<td>Matrix</td>
</tr>
<tr>
<td>2 M HCl</td>
<td>5.5</td>
<td>Matrix</td>
</tr>
<tr>
<td>8 M HCl</td>
<td>5.5</td>
<td>Ag</td>
</tr>
<tr>
<td>0.5 M HNO₃-0.1M HBr</td>
<td>5.5</td>
<td>Zn and Sn</td>
</tr>
<tr>
<td>2 M HNO₃</td>
<td>5.5</td>
<td>Cd</td>
</tr>
<tr>
<td>evaporte to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 8M HCl/scratch for 24 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporate to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 1 mL 0.7M HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AG-MP1 resin</td>
<td>100 µL</td>
<td></td>
</tr>
<tr>
<td>2 M HNO₃ (resin cleaning)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Mili-Q water (resin cleaning)</td>
<td>50 µL</td>
<td></td>
</tr>
<tr>
<td>8 M HCl (conversion to Cl⁻ form, wash)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (resin conditioning, wash)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>0.7 M HCl (sample solution)</td>
<td>1.6</td>
<td>Matrix</td>
</tr>
<tr>
<td>0.7 M HCl</td>
<td>1.6</td>
<td>Matrix</td>
</tr>
<tr>
<td>2 M HNO₃-0.1 M HBr</td>
<td>1.6</td>
<td>Zn and Sn</td>
</tr>
<tr>
<td>2 M HNO₃</td>
<td>1.6</td>
<td>Cd</td>
</tr>
<tr>
<td>evaporte to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reflux in H₂O₂ for 24 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>evaporte to dryness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolve in 2% HNO₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Cadmium isotopic measurements of the NIST 3108 standard during a single analytical session. During this session, the average 2 SE uncertainty for individual measurements is ±0.049 δ and is comparable to the 2 SD external reproducibility (±0.044 δ) based on repeat measurements of this standard.
Supplementary Methods 2 (Sequential extraction)

3.0 g of air dried and sieved (< 2mm) soil sample was digested following the steps in Table S2. After each extraction, the samples were centrifuged (4000 rpm) for 10 minutes and the reagents were pipetted out of the tube without any filtration and transferred to clean tubes for ICP-MS analysis. Before each extraction step, the remaining solid residue from the previous step was washed using 10 mL deionized water and the washings were discarded after centrifugation at 4000 rpm for 10 minutes.

Table S2. Sequential extraction method procedure

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Reagent</th>
<th>Extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>25 mL of 0.5 M MgCl₂ (pH 7)</td>
<td>1.5 h at 50°C</td>
</tr>
<tr>
<td>Bound to carbonates</td>
<td>25 mL of 0.5 M NaOAC (pH 5)</td>
<td>1.5 h at 50°C</td>
</tr>
<tr>
<td>Bound to Fe-Mn oxides</td>
<td>25 mL of 0.04 M Nh₂OH-Hcl in 25% (v/v) HOAC</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td>Bound to organic matter</td>
<td>4.5 mL of 0.02 M HNO₃ and 7.2 mL of H₂O₂ (pH 2 with HNO₃)</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td></td>
<td>Add 4.5 mL of H₂O₂ (pH 2 with HNO₃)</td>
<td>1.5 h at 85°C</td>
</tr>
<tr>
<td></td>
<td>Add 8.8 mL of 3.2 M NH₄OAC in 20% (v/v) HNO₃</td>
<td>30 min at room temperature</td>
</tr>
<tr>
<td>Residual</td>
<td>4 mL Aqua Regia</td>
<td>Salmanzadeh, et al.¹</td>
</tr>
</tbody>
</table>

Figure S2. The percentage of Cd in different fractions of topsoil 2015
Supplementary Methods 3 (pH adsorption edge experiment)

Native (unfertilized) soil samples were air dried and sieved (< 2mm). 1 g of soil sample was added to a set of beakers containing 100 ml of 0.01 M NaNO3 and then Cd(NO3)2 was added at the concentration of $1 \times 10^{-4}$ M. Eleven pH values were covered from 3.5-8.5 using NaOH or HNO3. After shaking the samples at 150 rpm on a reciprocating shaker for 24 h at room temperature (20 °C), samples were filtered using a 0.45 µm membrane filters and then Cd concentration was measured using ICP-MS2.

![Figure S3. Adsorption of $1 \times 10^{-4}$ M Cd onto Winchmore soils](image-url)
Table S3. Cd concentration and isotope compositions of Cd for all individual topsoil, fertilizer, phosphorite and control subsoil samples, where data are available for two independently processed replicate aliquots

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd (mg kg(^{-1}))^(a)</th>
<th>(\delta^{114/110})Cd ± 2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native (unfertilized) subsoil-1</td>
<td>0.02</td>
<td>-0.36 ± 0.05</td>
</tr>
<tr>
<td>Native (unfertilized) subsoil-2</td>
<td>0.02</td>
<td>-0.31 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1959-1</td>
<td>0.16</td>
<td>0.23 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1959-2</td>
<td>0.15</td>
<td>0.31 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1961-1</td>
<td>0.21</td>
<td>0.09 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1961-2</td>
<td>0.23</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1967-1</td>
<td>0.25</td>
<td>0.18 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1967-2</td>
<td>0.22</td>
<td>0.22 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1974-1</td>
<td>0.23</td>
<td>0.15 ± 0.08</td>
</tr>
<tr>
<td>Topsoil 1974-2</td>
<td>0.23</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>Topsoil 1979-1</td>
<td>0.25</td>
<td>0.20 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 1979-2</td>
<td>0.25</td>
<td>0.25 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 1986-1</td>
<td>0.30</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1986-2</td>
<td>0.27</td>
<td>0.17 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1993-1</td>
<td>0.34</td>
<td>0.15 ± 0.06</td>
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<tr>
<td>Topsoil 1993-2</td>
<td>0.46</td>
<td>0.09 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 1999-1</td>
<td>0.35</td>
<td>0.19 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 1999-2</td>
<td>0.35</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2002-1</td>
<td>0.38</td>
<td>0.19 ± 0.06</td>
</tr>
<tr>
<td>Topsoil 2002-2</td>
<td>0.31</td>
<td>0.14 ± 0.07</td>
</tr>
<tr>
<td>Topsoil 2004-1</td>
<td>0.28</td>
<td>0.09 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2004-2</td>
<td>0.29</td>
<td>Not Reported(^b)</td>
</tr>
<tr>
<td>Topsoil 2009-1</td>
<td>0.29</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2009-2</td>
<td>0.29</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2015-1</td>
<td>0.30</td>
<td>0.19 ± 0.05</td>
</tr>
<tr>
<td>Topsoil 2015-2</td>
<td>0.31</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>Fertilizer 1980s-1</td>
<td>30.7</td>
<td>0.24 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 1980s-2</td>
<td>33.0</td>
<td>0.25 ± 0.05</td>
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<tr>
<td>Fertilizer 2000-1</td>
<td>26.9</td>
<td>0.19 ± 0.06</td>
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<tr>
<td>Fertilizer 2000-2</td>
<td>27.1</td>
<td>0.16 ± 0.06</td>
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<tr>
<td>Fertilizer 2007-1</td>
<td>23.3</td>
<td>-0.14 ± 0.06</td>
</tr>
<tr>
<td>Fertilizer 2007-2</td>
<td>23.4</td>
<td>-0.09 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 2015-1</td>
<td>8.34</td>
<td>-0.18 ± 0.05</td>
</tr>
<tr>
<td>Fertilizer 2015-2</td>
<td>8.20</td>
<td>-0.17 ± 0.04</td>
</tr>
<tr>
<td>Nauru phosphorite-2</td>
<td>92.2</td>
<td>0.28 ± 0.06</td>
</tr>
<tr>
<td>Nauru phosphorite-2</td>
<td>100.0</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>Christmas Island phosphorite-1</td>
<td>35.2</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>Christmas Island phosphorite-2</td>
<td>40.7</td>
<td>0.18 ± 0.06</td>
</tr>
</tbody>
</table>

\(^{a}\) Instrumental uncertainties are ±0.9 % (2 SE) \(^{b}\) Due to value exceeding 2σ from the centroid
Table S4. Input data for the CadBal model in our study and McDowell 3 for the dryland treatment of the Winchmore long-term irrigation trial

<table>
<thead>
<tr>
<th>Input</th>
<th>McDowell 3</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farm type</td>
<td>Sheep/beef</td>
<td>Sheep/beef</td>
</tr>
<tr>
<td>Pasture yield (kg DM ha(^{-1}) y(^{-1}))</td>
<td>Annual data from Rickard and McBride(^4) and Smith, et al.(^6)</td>
<td>6442 (average of pasture yield in dryland treatment from Rickard and McBride(^4))</td>
</tr>
<tr>
<td>Sediment yield (erosion) (kg ha(^{-1}) y(^{-1}))</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Soil group</td>
<td>Yellow-grey earth (Silt loam)</td>
<td>Yellow-grey earth (Silt loam)</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>Sample depth (m)</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>Initial soil Cd (mg kg(^{-1}))</td>
<td>0.06</td>
<td>0.02 (control soil Cd)</td>
</tr>
<tr>
<td>P fertilizer rate (kg P ha(^{-1}) y(^{-1}))</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>P fertilizer Cd (mg kg(^{-1}) P)</td>
<td>345 (1952-1968)</td>
<td><strong>first scenario</strong>: input data same as McDowell 3</td>
</tr>
<tr>
<td></td>
<td>325 (1968-1975)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>155 (1975-1983)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>325 (1983-1996)</td>
<td><strong>second scenario</strong>: this study and P fertilizer Cd (mg kg(^{-1}) P) of:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>281 (2000-2001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>152 (2001-2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>219 (2005-2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>243 (2007-2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>161 (2011-2013)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86 (2015-2030)</td>
</tr>
<tr>
<td>Leaching loss (mg ha(^{-1}) y(^{-1}))</td>
<td>160(^b)</td>
<td><strong>third scenario</strong>: input data same as first scenario for pre-1998 AD fertilizers and second scenario for post-1998 AD fertilizers</td>
</tr>
<tr>
<td>Atmospheric accession (mg ha(^{-1}) y(^{-1}))</td>
<td>170</td>
<td><strong>fourth scenario</strong>: input data same as first scenario for pre-1998 AD fertilizers and second scenario for post-1998 AD fertilizers and leaching loss rate of 3200 mg ha(^{-1}) y(^{-1}) for post-2000 AD soils</td>
</tr>
</tbody>
</table>

\(^a\) (mg Cd kg\(^{-1}\) P) × (P% in fertilizer) ÷ 100 = mg Cd/kg fertilizer (P% ≈ 9%) \(^7\)
\(^b\) Calculated using the method and data from McDowell \(^3\),\(^8\) and Gray, et al. \(^9\), leaching loss = 1080 (Cd leaching from Brown soil \(^9\)) × [40 (olsen P from Winchmore soil-dryland treatment \(^8\)) / 27 (olsen P for Brown soil \(^3\))]
Supplementary Methods 4 (isotope mass balance)

The input and output terms in this mass balance were constrained using CadBal which generates loss terms for these vectors. This modelling utilized $\alpha$ values taken from Wiggenhauser, et al.\textsuperscript{10} which were selected on the basis of relevance (i.e. similarity to soil properties). Wiggenhauser, et al.\textsuperscript{10} showed that the isotope ratios of Cd ($^{114}/^{110}\delta$) in topsoil (Qen soil, Silt loam) and plant (wheat) root were 0.07‰ and 0.11‰, respectively and the fractionation of Cd between whole plant (wheat) and extractable Cd (extracted using Ca(NO$_3$)$_2$ was $\Delta_{\text{extract-wheat}} = -0.03$‰.

Extractable Cd was introduced as available Cd (therefore available for leaching, plant uptake and erosion). Because erosion was considered negligible in our study (Plot 15, dryland treatment), the available Cd is considered to represent the Cd fraction available for plant uptake and leaching, and therefore $\Delta_{\text{extract-wheat}}$ defines the Cd isotope fractionation in leachate. Therefore:

$$\delta_{\text{plant-topsoil}} = \frac{\delta_{\text{plant}} + 1000}{\delta_{\text{soil}} + 1000} = \frac{0.11 + 1000}{0.07 + 1000} = 1.00004$$

And

$$\alpha_{\text{leaching-topsoil}} = \frac{\delta_{\text{leaching}} + 1000}{\delta_{\text{soil}} + 1000} = \frac{-0.03 + 1000}{0.07 + 1000} = 0.9999$$

We also examined the effect of using the entire Ca(NO$_3$)$_2$-extractable fraction (without plant uptake) to represent the leached Cd. This resulted in very large differences to composition of the leached fraction calculated using the CadBal outputs, and an unrealistically negative soil isotope composition. Using these $\alpha$ values and Equations 3 and 4 (in the main manuscript), we estimated the isotope ratios of Cd in topsoil and in soil leachate through the interval of the Winchmore
field trial, and beyond (Figure 3). In addition, we applied the factor of 0.37 (the percentage of available Cd in our soil samples based on the sequential extraction; Figure S2) to our mass balance model. The results of this exercise also showed a negligible difference to the results from using total Cd concentrations in the soil and are therefore not given herein.

**Matlab code**

**Soil 1959-1993**

```matlab
>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> %of_ratio=isotope ratio of old fertiliser
>> vals=csvread('3-pre2000-1.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> of_ratio=vals(1,5);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %fof=fraction of old fertiliser
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for old fertiliser source
>> sigma_fof=0.18;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> fof_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fof_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fof_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
```
>> fnfof_corr=zeros(size(concentration));
>> % determines best outcomes or values with the highest likelihood of being true
for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
    % choose f so that sum(f)=1 -> use fn to find fof
    fn_trial=unifrnd(0,1,N,1);
    pos=find(fn_trial<=1);
    fn_trial=fn_trial(pos);
    fof_trial=1-(fn_trial);
    % generate random samples of sample ratio
    n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
    of_ratio_trial=normrnd(of_ratio,sigma_fof,length(pos),1);
    % predicted sample isotope ratio
    sa_ratiop=(fn_trial.*n_ratio_trial)+(fof_trial.*of_ratio_trial);
    % L2^2 norm
    phi=(sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
    % determines best outcomes or values with the highest likelihood of being true
    [best_phi,pos]=min(phi);
    fn_best(n)=fn_trial(pos);
    fof_best(n)=fof_trial(pos);
    sa_ratiop_best(n)=sa_ratiop(pos);
    % GaussianDataError
    L=exp((-1/2).*phi); L=L./max(L);
    accept=find(L>=rand(size(L)));
    fprintf(1,['year %y: tried %y samples of the prior, accepted %y',
               ' samples of the posterior; %6.2f%% acceptance
'],n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));
    % isolates and determines accepted posteriors values for function
    % contributions from natural soil, and old fertiliser
    phi_post=phi(accept);
    fn_post=fn_trial(accept);
    fof_post=fof_trial(accept);
    % isolates and determines accepted posterior values of isotope ratios of sources
    n_ratio_post=n_ratio_trial(accept);
    of_ratio_post=of_ratio_trial(accept);
    % saves accepted values to folder
    save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','fof_post','n_ratio_post','of_ratio_post');
    fn_mean(n)=mean(fn_trial(accept));
    fof_mean(n)=mean(fof_trial(accept));
    Cmat=cov([fn_trial(accept) fof_trial(accept)]);
    fn_std(n)=sqrt(Cmat(1,1));
    fof_std(n)=sqrt(Cmat(2,2));
    % determines covariance relationships between the posterior fraction contribution
    values from different sources
    fnfof_corr(n)=Cmat(1,2)/(fn_std(n)*fof_std(n));
end
Soil 1993
>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> %of_ratio=isotope ratio of old fertiliser and fertiliser 1998
>> vals=csvread('3-pre2000-2.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> of_ratio=vals(1,5);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %fof=fraction of fertilisers
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for two fertiliser sources
>> sigma_fof=0.15;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> fof_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fof_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fof_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnfof_corr=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
  %choose f so that sum(f)=1 -> use fn to find fof
  fn_trial=unifrnd(0,1,N,1);
  pos=find(fn_trial<=1);
  fn_trial=fn_trial(pos);
  fof_trial=1-(fn_trial);
  n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
  of_ratio_trial=normrnd(of_ratio,sigma_fof,length(pos),1);
  %predicted sample isotope ratio
  n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
  of_ratio_trial=normrnd(of_ratio,sigma_fof,length(pos),1);
  %predicted sample isotope ratio
sa_ratiop = (fn_trial.*n_ratio_trial)+(fof_trial.*of_ratio_trial);

\%L2^2 norm
phi = (sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
\%determines best outcomes or values with the highest likelihood of being true
[best_phi,pos] = min(phi);
fn_best(n) = fn_trial(pos);
fof_best(n) = fof_trial(pos);
sa_ratiop_best(n) = sa_ratiop(pos);

\%GaussianDataError
L = exp((-1/2).*phi); L = L./max(L);
accept = find(L >= rand(size(L)));

fprintf(1,
'year %y: tried %y samples of the prior, accepted %y,\% acceptance rate; %6.2f\% acceptance rate
'],n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));

\%isolates and determines accepted posteriors values for function
\%contributions from natural soil, and old fertiliser
phi_post = phi(accept);
fn_post = fn_trial(accept);
fof_post = fof_trial(accept);

\%isolates and determines accepted posterior values of isotope ratios of sources
n_ratio_post = n_ratio_trial(accept);
of_ratio_post = of_ratio_trial(accept);

\%saves accepted values to folder
save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','fof_post','n_ratio_post','of_ratio_post');

fn_mean(n) = mean(fn_trial(accept));
fof_mean(n) = mean(fof_trial(accept));
Cmat = cov([fn_trial(accept) fof_trial(accept)]);
fn_std(n) = sqrt(Cmat(1,1));
fof_std(n) = sqrt(Cmat(2,2));

\%determines covariance relationships between the posterior fraction contribution values from different sources
fnfof_corr(n) = Cmat(1,2)/(fn_std(n)*fof_std(n));
end
Soil 2002 and 2004

>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> %f2001_ratio=isotope ratio of fertiliser 2001
>> vals=csvread('2-post2000-1.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> fpr2000_ratio=vals(1,5);
>> f2001_ratio=vals(1,6);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %ffpr2000=fraction of pre-2000 fertilisers
>> %ff2001=fraction of fertiliser 2001
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for pre-2000 fertilisers
>> sigma_ffpr2000=0.18;
>> %designated errors for post 2000 fertilisers
>> sigma_ff2001=0.25;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> ffpr2000_best=zeros(size(concentration));
>> ff2001_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> ffpr2000_mean=zeros(size(concentration));
>> ff2001_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> ffpr2000_std=zeros(size(concentration));
>> ff2001_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnffpr2000_corr=zeros(size(concentration));
>> fnff2001_corr=zeros(size(concentration));
>> ffpr2000ff2001_corr=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
>> for n=sample_number
%choose f so that sum(f)=1 -> use fn and ffpr2000 to find ff2001
fn_trial=unifrnd(0,1,N,1);
ffpr2000_trial=unifrnd(0,1,N,1);
pos=find(fn_trial+ffpr2000_trial<=1);
fn_trial=fn_trial(pos);
ffpr2000_trial=ffpr2000_trial(pos);
ff2001_trial=1-(fn_trial+ffpr2000_trial);
%generate random samples of sample ratio
n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
ffpr2000_ratio_trial=normrnd(ffpr2000_ratio,sigma_ffpr2000,length(pos),1);
f2001_ratio_trial=normrnd(f2001_ratio,sigma_ff2001,length(pos),1);
%predicted sample isotope ratio
sa_ratiop=(fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ff2001_trial.*f2001_ratio_trial);
%L2^2 norm
phi=(sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
%determines best outcomes or values with the highest likelihood of being true
[best_phi,pos]=min(phi);
fn_best(n)=fn_trial(pos);
ffpr2000_best(n)=ffpr2000_trial(pos);
ff2001_best(n)=ff2001_trial(pos);
%saves accepted values to folder
save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','ffpr2000_post','ff2001_post','n_ratio_post','fpr2000_ratio_post','f2001_ratio_post');
fn_mean(n)=mean(fn_trial(accept));
ffpr2000_mean(n)=mean(ffpr2000_trial(accept));
ff2001_mean(n)=mean(ff2001_trial(accept));
Cmat=cov([fn_trial(accept) ffpr2000_trial(accept) ff2001_trial(accept)]);
fn_std(n)=sqrt(Cmat(1,1));
ffpr2000_std(n)=sqrt(Cmat(2,2));
ff2001_std(n)=sqrt(Cmat(3,3));
% determines covariance relationships between the posterior fraction contribution values from different sources
fnffpr2000_corr(n)=Cmat(1,2)/(fn_std(n)*ffpr2000_std(n));
fnff2001_corr(n)=Cmat(1,3)/(fn_std(n)*ff2001_std(n));
ffpr2000ff2001_corr(n)=Cmat(2,3)/(ffpr2000_std(n)*ff2001_std(n));
end
Soil 2009
>> %year=year of sampling
>> %concentration=Cd concentrations
>> %sa_ratio=isotope ratio of mixed sample
>> %n_ratio=isotope ratio of natural soil
>> vals=csvread('2-post2000-2.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> fpr2000_ratio=vals(1,5);
>> fpo2000_ratio=vals(1,6);
>> %designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> %N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> %fractions of source definitions
>> %fn=fraction of natural soil
>> %ffpr2000=fraction of pre-2000 fertilisers
>> %ffpo2000=fraction of post 2000 fertilisers
>> %designated errors for natural soil source
>> sigma_fn=0.2;
>> %designated errors for pre-2000 fertilisers
>> sigma_ffpr2000=0.18;
>> %designed errors for post 2000 fertilisers
>> sigma_ffpo2000=0.20;
>> %arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> fpr2000_best=zeros(size(concentration));
>> fpo2000_best=zeros(size(concentration));
>> %arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fpr2000_mean=zeros(size(concentration));
>> fpo2000_mean=zeros(size(concentration));
>> %arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fpr2000_std=zeros(size(concentration));
>> fpo2000_std=zeros(size(concentration));
>> %arrays to keep the 2D correlation coefficients of the posteriors
>> fnfpr2000_corr=zeros(size(concentration));
>> fnfpo2000_corr=zeros(size(concentration));
>> fpr2000fpo2000_corr=zeros(size(concentration));
>> %determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratiop_best=zeros(size(concentration));
for n=sample_number
%
choose f so that sum(f)=1 -> use fn and ffpr2000 to find ffpo2000
fn_trial=unifrnd(0,1,N,1);
ffpr2000_trial=unifrnd(0,1,N,1);
pos=find(fn_trial+ffpr2000_trial<=1);
fn_trial=fn_trial(pos);
ffpr2000_trial=ffpr2000_trial(pos);
ffpo2000_trial=1-(fn_trial+ffpr2000_trial);
%
generate random samples of sample ratio
n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
ffpr2000_ratio_trial=normrnd(fpr2000_ratio,sigma_ffpr2000,length(pos),1);
ffpo2000_ratio_trial=normrnd(fpo2000_ratio,sigma_ffpo2000,length(pos),1);
%
predicted sample isotope ratio
sa_ratiop=(fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ffpo2000_trial.*fpo2000_ratio_trial);
%
L2^2 norm
phi=(sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
%
determines best outcomes or values with the highest likelihood of being true
[best_phi,pos]=min(phi);
fn_best(n)=fn_trial(pos);
ffpr2000_best(n)=ffpr2000_trial(pos);
ffpo2000_best(n)=ffpo2000_trial(pos);
%
%%GaussianDataError%%%
L=exp((-1/2).*phi); L=L./max(L);
accept=find(L>=rand(size(L)));
fprintf(1,['year %y: tried %y samples of the prior, accepted %y samples of the posterior; %6.2f% acceptance rate\n'],n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));
%
isolates and determines accepted posteriors values for function
%
phi_post=phi(accept);
fn_post=fn_trial(accept);
ffpr2000_post=ffpr2000_trial(accept);
ffpo2000_post=ffpo2000_trial(accept);
%
isolates and determines accepted posterior values of isotope ratios of sources
n_ratio_post=n_ratio_trial(accept);
ffpr2000_ratio_post=ffpr2000_ratio_trial(accept);
ffpo2000_ratio_post=ffpo2000_ratio_trial(accept);
%
saves accepted values to folder
save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','ffpr2000_post','ffpo2000_post'
','n_ratio_post','ffpr2000_ratio_post','ffpo2000_ratio_post');
fn_mean(n)=mean(fn_trial(accept));
ffpr2000_mean(n)=mean(ffpr2000_trial(accept));
ffpo2000_mean(n)=mean(ffpo2000_trial(accept));
Cmat=cov([fn_trial(accept) ffpr2000_trial(accept) ffpo2000_trial(accept)]);
fn_std(n)=sqrt(Cmat(1,1));
ffpr2000_std(n)=sqrt(Cmat(2,2));
ffpo2000_std(n)=sqrt(Cmat(3,3));
% determines covariance relationships between the posterior fraction contribution values from different sources

\[ fn\text{ffpr2000}_\text{corr}(n) = \frac{\text{Cmat}(1,2)}{\text{fn}_\text{std}(n)\text{ffpr2000}_\text{std}(n)}; \]

\[ fn\text{ffpo2000}_\text{corr}(n) = \frac{\text{Cmat}(1,3)}{\text{fn}_\text{std}(n)\text{ffpo2000}_\text{std}(n)}; \]

\[ \text{ffpr2000ffpo2000}_\text{corr}(n) = \frac{\text{Cmat}(2,3)}{\text{ffpr2000}_\text{std}(n)\text{ffpo2000}_\text{std}(n)}; \]

end
Soil 2015

>> year=year of sampling
>> concentration=Cd concentrations
>> ssa_ratio=isotope ratio of mixed sample
>> n_ratio=isotope ratio of natural soil
>> vals=csvread('2-post2000-3.csv',1,0);
>> year=vals(:,1);
>> concentration=vals(:,2);
>> sa_ratio=vals(:,3);
>> n_ratio=vals(1,4);
>> fpr2000_ratio=vals(1,5);
>> fpo2000_ratio=vals(1,6);
>> designated error for isotope ratios of sample
>> sigma_sa=0.2;
>> N is number of model trial run
>> N=1e5;
>> sample_number=[1:size(vals,1)];
>> fractions of source definitions
>> fn=fraction of natural soil
>> fpfpr2000=fraction of pre-2000 fertilisers
>> ffp2000=fraction of post 2000 fertilisers
>> designated errors for natural soil source
>> sigma_fn=0.2;
>> designated errors for pre-2000 fertilisers
>> sigma_ffpr2000=0.18;
>> designated errors for post 2000 fertilisers
>> sigma_ffpo2000=0.29;
>> arrays to keep the best outcomes or values with the highest likelihood of being true for fraction contribution from end members
>> fn_best=zeros(size(concentration));
>> fpfpr2000_best=zeros(size(concentration));
>> ffp2000_best=zeros(size(concentration));
>> arrays to keep the mean of posterior, or the average fraction contribution from end members
>> fn_mean=zeros(size(concentration));
>> fpfpr2000_mean=zeros(size(concentration));
>> ffp2000_mean=zeros(size(concentration));
>> arrays to keep the standard deviations of the posteriors
>> fn_std=zeros(size(concentration));
>> fpfpr2000_std=zeros(size(concentration));
>> ffp2000_std=zeros(size(concentration));
>> arrays to keep the 2D correlation coefficients of the posteriors
>> fnfpfpr2000_corr=zeros(size(concentration));
>> fnffpo2000_corr=zeros(size(concentration));
>> fpfpr2000ffpo2000_corr=zeros(size(concentration));
>> determines best outcomes or values with the highest likelihood of being true for isotope ratios
>> sa_ratio_best=zeros(size(concentration));
for n=sample_number
  %choose f so that sum(f)=1 -> use fn and ffpr2000 to find ffpo2000
  fn_trial=unifrnd(0,1,N,1);
  ffpr2000_trial=unifrnd(0,1,N,1);
  pos=find(fn_trial+ffpr2000_trial<=1);
  fn_trial=fn_trial(pos);
  ffpr2000_trial=ffpr2000_trial(pos);
  ffpo2000_trial=1-(fn_trial+ffpr2000_trial);
  %generate random samples of sample ratio
  n_ratio_trial=normrnd(n_ratio,sigma_fn,length(pos),1);
  fpr2000_ratio_trial=normrnd(fpr2000_ratio,sigma_ffpr2000,length(pos),1);
  fpo2000_ratio_trial=normrnd(fpo2000_ratio,sigma_ffpo2000,length(pos),1);
  %predicted sample isotope ratio
  sa_ratiop=(fn_trial.*n_ratio_trial)+(ffpr2000_trial.*fpr2000_ratio_trial)+(ffpo2000_trial.*fpo2000_ratio_trial);
  %L2^2 norm
  phi=(sa_ratiop-sa_ratio(n)).^2./sigma_sa.^2;
  %determines best outcomes or values with the highest likelihood of being true
  [best_phi,pos]=min(phi);
  fn_best(n)=fn_trial(pos);
  ffpr2000_best(n)=ffpr2000_trial(pos);
  ffpo2000_best(n)=ffpo2000_trial(pos);
  sa_ratiop_best(n)=sa_ratiop(pos);
  %GaussianDataError%
  L=exp((-1/2).*phi); L=L./max(L);
  accept=find(L>=rand(size(L)));
  fprintf(1,'[year %y: tried %y samples of the prior, accepted %y samples of the posterior; %6.2f\% acceptance rate\n]',n,length(fn_trial),length(accept),100*length(accept)/length(fn_trial),char(37));
  %isolates and determines accepted posteriors values for function
  %contributions from natural soil, and old fertiliser
  phi_post=phi(accept);
  fn_post=fn_trial(accept);
  ffpr2000_post=ffpr2000_trial(accept);
  ffpo2000_post=ffpo2000_trial(accept);
  %isolates and determines accepted posterior values of isotope ratios of sources
  n_ratio_post=n_ratio_trial(accept);
  fpr2000_ratio_post=fpr2000_ratio_trial(accept);
  fpo2000_ratio_post=fpo2000_ratio_trial(accept);
  %saves accepted values to folder
  save(sprintf('Post_%02d.mat',n),'phi_post','fn_post','ffpr2000_post','ffpo2000_post',
           'n_ratio_post','fpr2000_ratio_post','fpo2000_ratio_post');
  fn_mean(n)=mean(fn_trial(accept));
  ffpr2000_mean(n)=mean(ffpr2000_trial(accept));
  ffpo2000_mean(n)=mean(ffpo2000_trial(accept));
  Cmat=cov([fn_trial(accept) ffpr2000_trial(accept) ffpo2000_trial(accept)]);
  fn_std(n)=sqrt(Cmat(1,1));
  ffpr2000_std(n)=sqrt(Cmat(2,2));
  ffpo2000_std(n)=sqrt(Cmat(3,3));
determines covariance relationships between the posterior fraction contribution values from different sources

\[
\begin{align*}
\text{fnffpr2000\_corr}(n) &= \frac{\text{Cmat}(1,2)}{\text{fn\_std}(n)\times\text{ffpr2000\_std}(n)}; \\
\text{fnffpo2000\_corr}(n) &= \frac{\text{Cmat}(1,3)}{\text{fn\_std}(n)\times\text{ffpo2000\_std}(n)}; \\
\text{ffpr2000ffpo2000\_corr}(n) &= \frac{\text{Cmat}(2,3)}{\text{ffpr2000\_std}(n)\times\text{ffpo2000\_std}(n)};
\end{align*}
\]
end
References

Co-Authorship Form

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<tr>
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<th>Sampling, conducted experiment, and data analysis, including figures creation. Wrote the manuscript/thesis chapter.</th>
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<tbody>
<tr>
<td>Extent of contribution by PhD candidate (%)</td>
<td>90%</td>
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CO-AUTHORS

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<tr>
<th>Name</th>
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<tr>
<td>Megan R. Balks</td>
<td>Project conception; provided comments and editing of versions of the manuscript, assisted with field work</td>
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<tr>
<td>Adam Hartland</td>
<td>Project conception and experiment design, provided comments and editing of the manuscript</td>
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<td>Secured funding, provided comments and editing of the manuscript</td>
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Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and

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Nature of contribution by PhD candidate: Conducted experiments, and data analysis. Wrote the manuscript/thesis chapter

Extent of contribution by PhD candidate (%): 80%

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<tr>
<td>Adam Hartland</td>
<td>Secured funding, project conception and experiment design, provided substantial comments and fundamental editing of numerous versions of the manuscript, provided fertiliser and rock phosphate samples and sampled soils from Winchmore, produced figures for the manuscript</td>
</tr>
<tr>
<td>Claudine H. Stirling</td>
<td>Experiment design, facilitated access to MC-ICP-MS at Otago University, provided substantial comments and editing of versions of the manuscript</td>
</tr>
<tr>
<td>Megan R. Balks</td>
<td>Provided rock phosphate sample, provided comments and editing of the manuscript</td>
</tr>
<tr>
<td>Louis A. Schipper</td>
<td>Provided archived Winchmore soil samples, provided comments and editing of the manuscript</td>
</tr>
<tr>
<td>Chaitanya Joshi</td>
<td>Assisted with Matlab coding</td>
</tr>
<tr>
<td>Ejin George</td>
<td>Conducted MC-ICP-MS experiment and analysis, provided comments and editing of versions of the manuscript</td>
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<td>Experiment design, provided comments and editing of the manuscript</td>
</tr>
<tr>
<td>Paul L. Mudge</td>
<td>Sampling, provided comments and editing of the manuscript</td>
</tr>
<tr>
<td>Ray A Littler</td>
<td>Advice on statistical methods and editing of the manuscript</td>
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