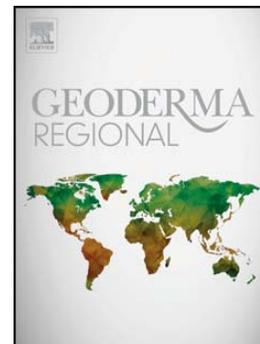# Accepted Manuscript

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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, Bruntwood 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.

Keywords: Cadmium accumulation, Agriculture, Pasture, New Zealand

1. Introduction

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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 less than 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

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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-Allopanic 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 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

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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 Allophanic 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 (Equation 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).

$$Cd = 0.000142 \text{ total P} + 0.042 \qquad \text{Equation (1)}$$

(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 ≥ 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.

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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 minerology 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 intergrade 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

Humaquept in US Soil Taxonomy) (Soil Survey Staff, 2014) 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) (Soil Survey Staff, 2014) is an intergrade 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).

Fig. 1. Here

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; Petruzzelli 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.

Table 1. Here

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 horizons (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 HNO_3 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 hr. After digestion, 50 mL of deionized water was pipetted into each digestion tube and the tubes were then centrifuged for 10 minutes at 4000 rpm and filtered at 0.45 microns (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 hours (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, Anglesey, U.K.) 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. Equation (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).

Fig. 2. Here

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.

Table 2. Here

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 (4.8-6.5) for the Brutwood soil and 5.8 (pH 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).

Fig. 3. Here

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).

Table 3. Here

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).

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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 $H_2PO_4^-$ at pH ~5.8) adsorbs strongly to allophane, whereas U (which mainly presents as $UO_2(CO_3)_2^{2-}$ at pH ~5.8) is generally more soluble.

Fig. 4. Here

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 4c). 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 4c).

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, significant positive correlation coefficients were found between P and some other elements including Cu and Zn (Table 4).

Fig. 5. Here

Table 4. Here

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 topsoils (mean of 0.74 mg kg^{-1}) (sampled from 2007 to 2013) (Stafford et al., 2014). The mean concentration of Cd in topsoils (0-7.5 cm) of Gley Soils (0.78 mg kg^{-1}, Te Kowhai) was greater than the mean concentration of Cd in topsoils (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 topsoils (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 reflects 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

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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 oxyhydroxides 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 adsorption 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 $\approx$ 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 allophanic 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

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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. Co, Cu, Zn and Mn can also be derived from superphosphate fertilizers (David et al., 1978; During, 1984; McLaughlin and Singh, 1999; Bolan et al., 2003; Reiser et al., 2014); therefore the correlation of P with Co, 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

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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 tospoils 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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Figure Captions

Fig. 1. Soils sampled in this study. Left: Horotiu (Orthic Allophanic Soil, Typic Hapludand), Centre: Bruntwood (Impeded Allophanic Soil, Aquic Hapludand) and Right: Te Kowhai (Orthic Gley Soil, Typic Humaquept).

Fig. 2. The mean concentrations (mg kg^{-1}) of Cd in different soil horizons (—•— total concentration, —o— estimated background concentration based on Equation 1, error bars are one standard deviation).

Fig. 3. Total mass of Cd (mg m^{-2}) to 60 cm depth in Horotiu, Bruntwood and Te Kowhai soils from Scott Farm, New Zealand (95% confidence interval).

Fig. 4. U/Cd, U/P and Cd/P ratios in soil samples from Scott Farm.

Fig. 5. Cluster analysis of phosphorus, pH and metals (A and B show two main clusters of elements probably originating from sources related to farming activities).
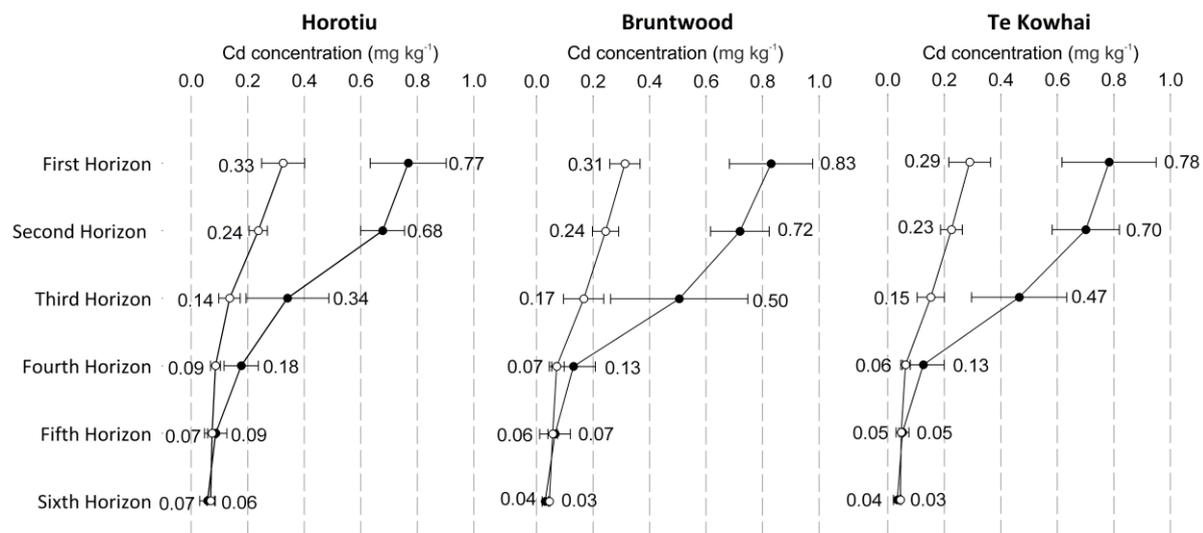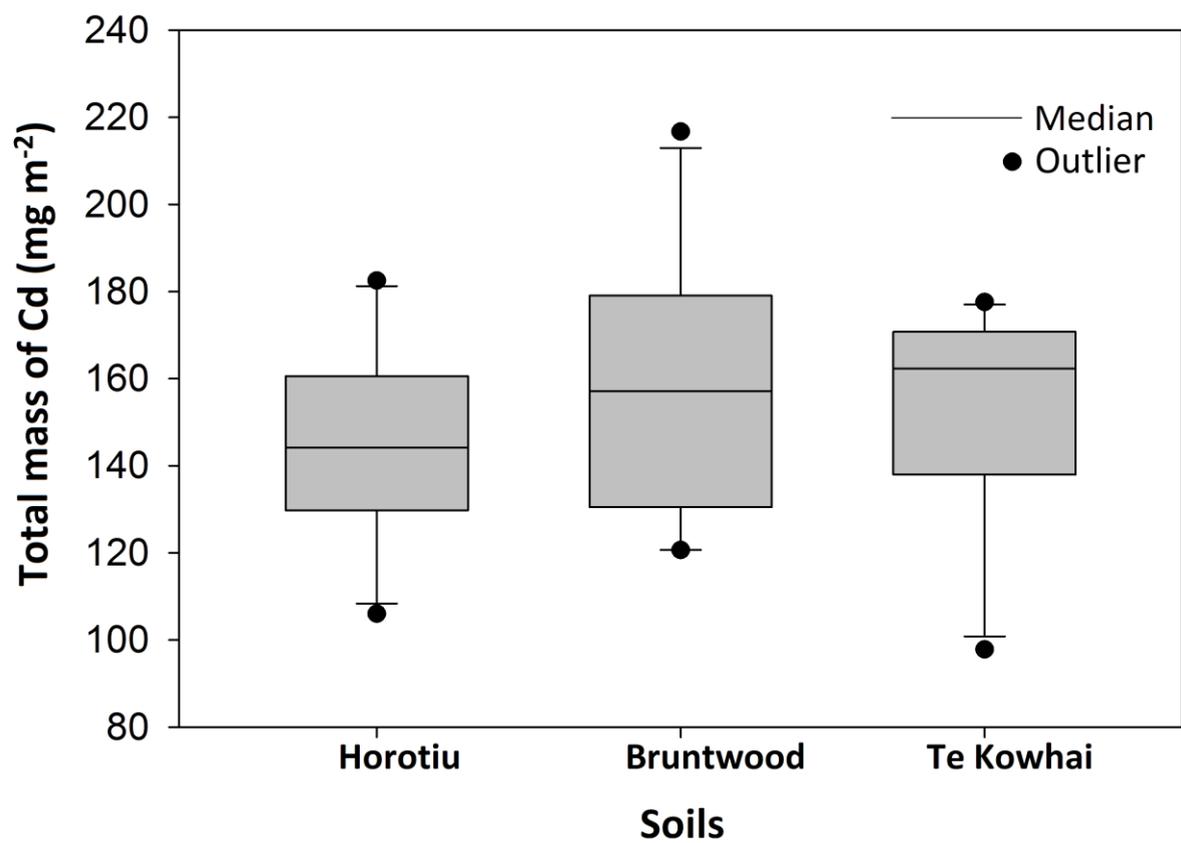
Figure 1

Figure 2

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Figure 3

Figure 4

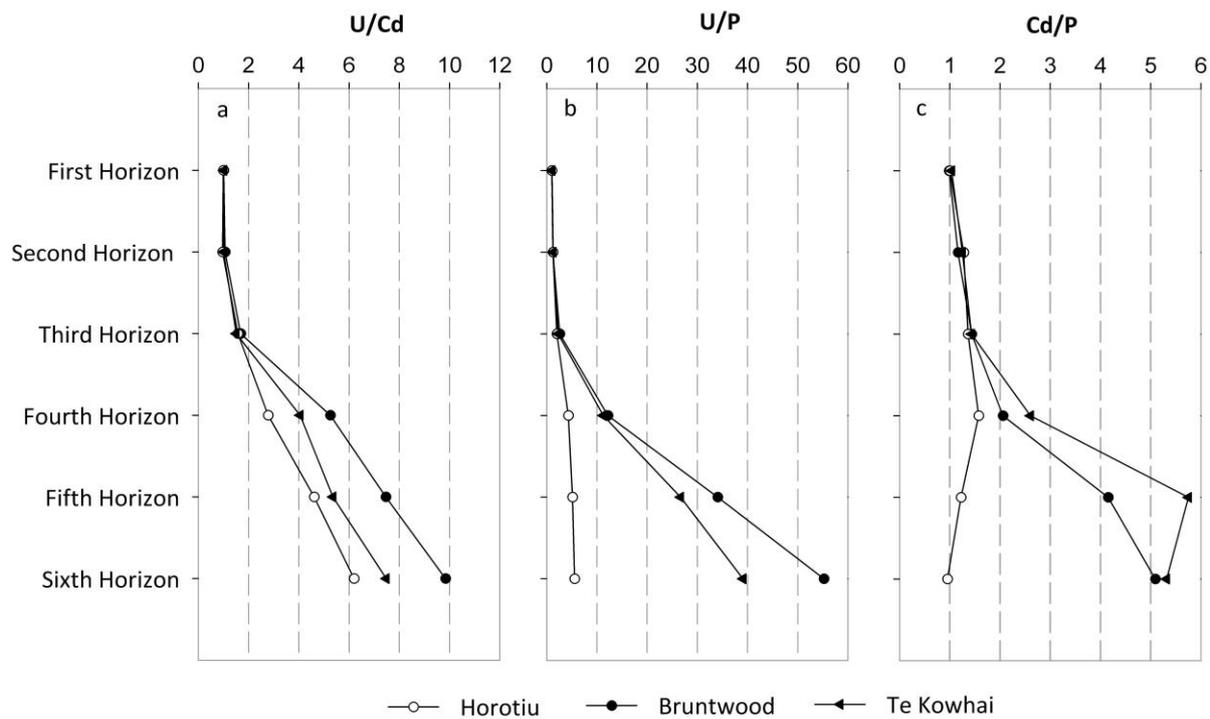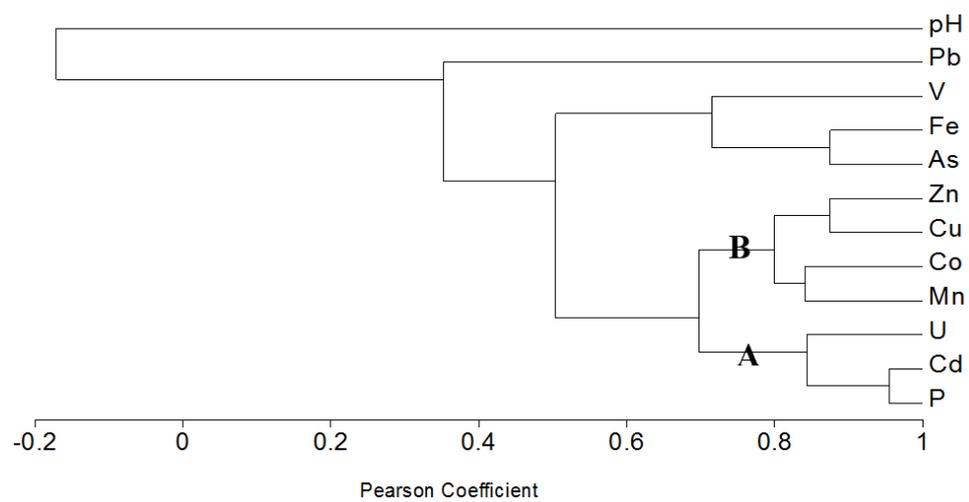Figure 5

Table 1. The fertilizer application history of Scott farm since 2000.

	Rate (kg ha^{-1})	Product	% Superphosphate	Rate of Superphosphate (kg ha^{-1})
Autumn 2000	650	Magnesium phosphate + (Selenium @ 1kg ton^{-1})		
Autumn 2001	700	Magnesium phosphate + (Selenium @ 1kg ton^{-1})		
Autumn 2002	650	Magnesium phosphate + (Selenium @ 1kg ton^{-1})		
Autumn 2003	600	Magnesium phosphate		
Autumn 2004	650	92% Superten + 8% Calcined Magnesite (CalMag)	92%	598
Autumn 2005	570	91% Superten + 4% Durasul Sulphur + 5% CalMag + 1 kg ha^{-1} Selcote Ultra	91%	519
Autumn 2006	570	91% Superten + 3% Durasul Sulphur + 5% CalMag + 1 kg ha^{-1} Selcote Ultra (1% Selenium)	91%	519
Autumn 2007	630	83% Superten + 8% Salt + 5% CalMag + 5% Durasul	83%	523
Autumn 2008	570	91% Superten + 5% Salt + 4% CalMag	91%	519
Autumn 2009	675	77% Superten + 8% Muriate of Potash + 7% Salt + 3% CalMag + 4% Durasul	77%	520
Autumn 2010	635	87% Superten + 8% Bulk Salt + 5% CalMag	87%	552
Autumn 2011	675	77% Superten + 8% Muriate of Potash + 7% Salt + 3% CalMag + 4% Durasul	77%	520
Autumn 2012	615	11% Superten + 81% Serpentine Super + 8% Summit Agricultural Salt (AgSalt) mix	11%	68
Autumn 2013	675	41% Superten + 82% Serpentine super + 7% AgSalt mix	41%	277
Autumn 2014	600	50% Serpentine Super + 50% Superten + 1 kg Selenium ha^{-1}	50%	300

Table 2. The mean concentration of elements (mg kg^{-1}) and pH in topsoil (0-15 cm) samples of this study and the Waikato region forest background (0-10 cm).

Elements	P	Cd	As	Pb	U	V	Fe	Mn	Co	Cu	Zn	pH
This study (range)	1622 (825-2809)	0.75 (0.44-1.11)	5 (2-9.7)	10.9 (8.8-14.2)	1.7 (1.1-2.4)	29.8 (11-64)	9856 (3839-21098)	429.3 (67-791)	2.9 (0.8-5.7)	11.3 (6.5-19.8)	66.6 (27-133)	5.8 (5.1-6.5)
Waikato region forest background (range)†	350 (160-730)	0.11 (0.03-0.3)	5.1 (1-25)	11 (3-32)	0.8 (0.2-2.5)	68 (5-300)	25600 (4700-76000)	780 (50-2960)	5.9 (0.9-28)	16 (4-55)	28 (11-58)	5.1 (4.2-6.0)

† from Taylor and Kim, 2009

Table 3. Mean of Cd concentration (mg kg^{-1}) in different fractions of topsoil (0-7.5 cm) samples from Horotiu, Bruntwood and Te Kowhai soil

	Exchangeable	Bound to Carbonates	Bound to Fe-Mn Oxides	Bound to Organic Matter	Residual
Horotiu	0.20	0.05	0.25	0.17	0.04
Bruntwood	0.20	0.05	0.25	0.17	0.04
Te Kowhai	0.20	0.05	0.24	0.15	0.04

Table 4. Pearson's correlation coefficient for elements and pH in soil samples (coefficients > 0.6 are underlined).

	P	Cd	As	Pb	U	V	Fe	Mn	Co	Cu	Zn	pH
P	1.000											
Cd	0.955[*]	1.000										
As	0.480	0.494	1.000									
Pb	0.263	0.340	0.374	1.000								
U	0.836[*]	0.852[*]	0.632[*]	0.519	1.000							
V	0.175	0.214	0.669[*]	0.120	0.312	1.000						
Fe	0.254	0.299	0.875[*]	0.342	0.447	0.760[*]	1.000					
Mn	0.643[*]	0.706[*]	0.681[*]	0.349	0.612[*]	0.342	0.597	1.000				
Co	0.509	0.580	0.796[*]	0.450	0.620[*]	0.525	0.767[*]	0.841[*]	1.000			
Cu	0.778[*]	0.776[*]	0.791[*]	0.393	0.816[*]	0.486	0.639[*]	0.784[*]	0.801[*]	1.000		
Zn	0.794[*]	0.794[*]	0.695[*]	0.377	0.745[*]	0.386	0.571	0.800[*]	0.816[*]	0.875[*]	1.000	
pH	-0.065	-0.076	-0.250	-0.210	-0.107	-0.053	-0.227	-0.266	-0.261	-0.243	-0.130	1.000

[*] $P < 0.01$

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Highlights

- Cd distribution was the same in contrasting soils with the same fertilizer history.

- Cd was retained in the topsoil with minimal movement to the subsoil.

- Cd fractionation was the same in different topsoils.

- Cd, P, and U were highly correlated suggesting a common fertilizer source.

- This study supports use of one Cd management tool for these soil types.

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