Concentrations of Selected Trace Elements for Various Land Uses and Soil Orders within Rural Auckland

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Concentrations of Selected Trace Elements for Various Land Use and Soil Orders within Rural Auckland

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Note: check of 2012 data

This report replaces the 2012 report, *Concentrations of selected trace elements for various land uses and soil orders within rural Auckland*, TR2012/021.

This 2015 report considers data for the same timeframe as the 2012 report. However, the data reported in 2012 contained errors which have been corrected in this 2015 report.

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Contents

Executive summary

Trace elements, naturally present in soils, are inherited from the parent material of the underlying rock as well as sea spray, dust and volcanic ash. However, concentrations of trace elements in soils are constantly being altered and are significantly influenced by the climate, land use and urban development. When trace element concentrations exceed recommended guidelines for soils they can have adverse effects on soil, plant and animal health. Trace elements can ultimately enter the food chain and/or be breathed in as dust resulting in impacts on human health.

Soil samples were collected across 84 sites within the Auckland region between periods 1999-00 and 2008-11, representing a total of 123 soil samples. Thirty-nine of the sites that were sampled between 1999-00 were also resampled between periods 2008-11. The 84 sites represented various land use types which included (with site numbers in parentheses) dairy (21), drystock (17), forestry (17), horticulture (18) and indigenous (11) land uses. The sites selected represented seven Soil Orders namely Allophanic (12), Brown (12), Gley (7), Granular (13), Organic (7), Recent (11) and Ultic (22). Soil samples was analysed for total recoverable arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn).

Although all trace element mean concentrations did not exceed recommended guidelines for environmental soil health, six of the 123 soil samples exceeded the guideline range which included (with number of samples in parentheses): arsenic (1), cadmium (4) and copper (1); and future monitoring will be important at these sites. These findings were comparable to those reported by other regional councils for rural soils in New Zealand.

Mean concentrations of trace elements were significantly different for land uses and Soil Orders. There were no significant differences between mean trace element concentrations in the 39 repeat sites that were sampled pre and post 2000, except for an increase in Ni.

Recommendations include the following:

- Re-sampling indigenous sites, which have not been influenced by anthropogenic activity, to provide up to date background concentrations for trace elements.

- Assessing and quantifying concentrations of trace elements in urban Auckland to determine how anthropogenic and industrial impacts might affect soil functional health within the urban environment.

- Consider determining trace elements on a volumetric basis (g/m^3) or using soil pools (g/m^2) to take account of soil types with differing bulk densities; otherwise the true levels of trace elements can be over- or under-estimated for soils with low and high bulk densities, respectively.

- Lastly, productive land use sites should be re-sampled every five years to identify changes in trace element concentrations between sites, especially those sites that currently exceed guidelines, and to establish trends. For sites that consistently exceed guidelines, land managers should advise and provide a suite of best management practices or develop a personal farm management plan for land owners to ensure the management of soil health.

1.0 Introduction

Trace elements, naturally present in soils, are inherited from the parent material of the underlying rock as well as sea spray, dust and volcanic ash. Soils with similar parent material typically have similar concentrations of trace elements and levels tend to be low (Longhurst et al., 2004). Environment Canterbury (2006) described background trace element concentrations as '*The naturally occurring concentration of trace elements attributable to the mineral content in the parent material of the soil and any modification due to the soil forming processes*'. Volcanic activity resulting in ore deposits has been reported to be a natural temporal source of cadmium, zinc, copper and lead (Godt et al., 2006) and greater concentrations of a suite of trace elements have been associated with volcanically derived soils (ARC, 2001). However, concentrations of trace elements in soils are constantly being altered and are significantly influenced by the climate, rural land use and the development of residential and urban areas (Gaw et al., 2006, Longhurst et al., 2004, Roberts et al., 1994).

There has been increasing concern in the elevation of trace element concentrations in soils in recent years which have resulted from the historical routine use of soil amendments and the increasing intensification of land use e.g. Longhurst et al. (2004) and Taylor et al. (2010). Consequently, several regional councils across New Zealand have begun to monitor and report the concentrations of trace elements across various soils and land uses within the past 10 years e.g. Auckland Regional Council (ARC, 2001), Marlborough District Council (Gray, 2011), Environment Canterbury (ECan, 2006) and Waikato Regional Council (Kim and Taylor, 2009). Not all trace elements are essential for plant health and animal growth. Non-essential elements include cadmium, lead and arsenic (to name a few), and their excessive accumulation can have detrimental impacts on soil, plant and animal health. Furthermore, elevated concentrations of such trace elements, in particular cadmium, have the potential to enter the food chain and continuous exposure can result in kidney, bone and pulmonary dysfunction (Godt et al., 2006). On the other hand, deficiencies of essential elements in soil can lead to health-related problems such as infectious diseases and malnutrition particularly in relation to inadequate supplies of iodine and zinc (Steinnes, 2010).

Apart from a study in 2006 (Gaw et al., 2006) that looked at trace element concentrations in horticultural soils in Auckland, no work has been conducted on trace element concentrations since the Auckland Regional Council (ARC) produced a report on the background concentrations of trace elements for Auckland in 2001 (ARC, 2001). Given that 90% of the Auckland region is considered to be rural land, the current report investigates the concentrations of trace elements for various land uses and Soil Orders in rural Auckland.

2.0 Materials and methods

2.1 Sample sites and soil sampling

Eighty-four sites, from a variety of land uses and Soil Orders, were sampled between 1999-00 and 2008-11 (Figure 1). Thirty-nine of these sites that were first sampled between 1999-00 were re-sampled between 2008-11 and the data reports on the total of 123 soil samples. These sites have also been used for the national '500 Soils Programme' that was initiated in 1995, whereby many regional councils commenced a national soil monitoring program (Hill and Sparling, 2009). However, after 2001 Auckland did not participate in further soil quality monitoring until 2008, hence a gap in soil sampling years. It was not possible to attain a complete archive of soil samples collected between 1995 and 2000, and only a selection of soil samples could be analysed prior to 2000. The sites sampled were representative of the region's land uses and Soil Orders. The land use activities included dairy, drystock, forestry, horticulture and indigenous forest and, excluding repeated sites, this consisted of 21, 17, 17, 18 and 11 sites for each land use, respectively. Horticulture includes viticulture, market garden vegetable production and orchards. The Soil Orders were identified as Allophanic (12 sites), Brown (12), Gley (7), Granular (13), Organic (7), Recent (11) and Ultic (22) following the New Zealand Soil Classification (Hewitt, 1998).

Soil samples were taken along a 50m transect at 2m intervals to a depth of 10cm using a bucket corer with a 2.5cm diameter (Hill and Sparling, 2009). The 25 individual cores collected were homogenised for chemical analysis at an IANZ-accredited laboratory (Watercare Laboratory Services).

Recommended guidelines for trace element concentrations are based on those reported in New Zealand Water and Wastes Association (2003) to align with findings from neighbouring councils which include Waikato Regional Council (Taylor et al., 2010) and Environment Bay of Plenty Regional Council (Guinto, 2011). However, background concentrations of trace elements reported for the former Auckland Regional Council (ARC, 2001) will also be highlighted for informative purposes. It should be noted that the latter were derived from soil samples collected in urban Auckland and are considered to be '*ambient background*' concentrations i.e. those that are representative of the area surrounding the sites (Cavanagh, 2013). These concentrations will differ from '*natural background*' levels which are typically collected from native bush sites with concentrations attributable to the mineral content derived from parent materials. Hence, there will be differences between the two (Table 2).

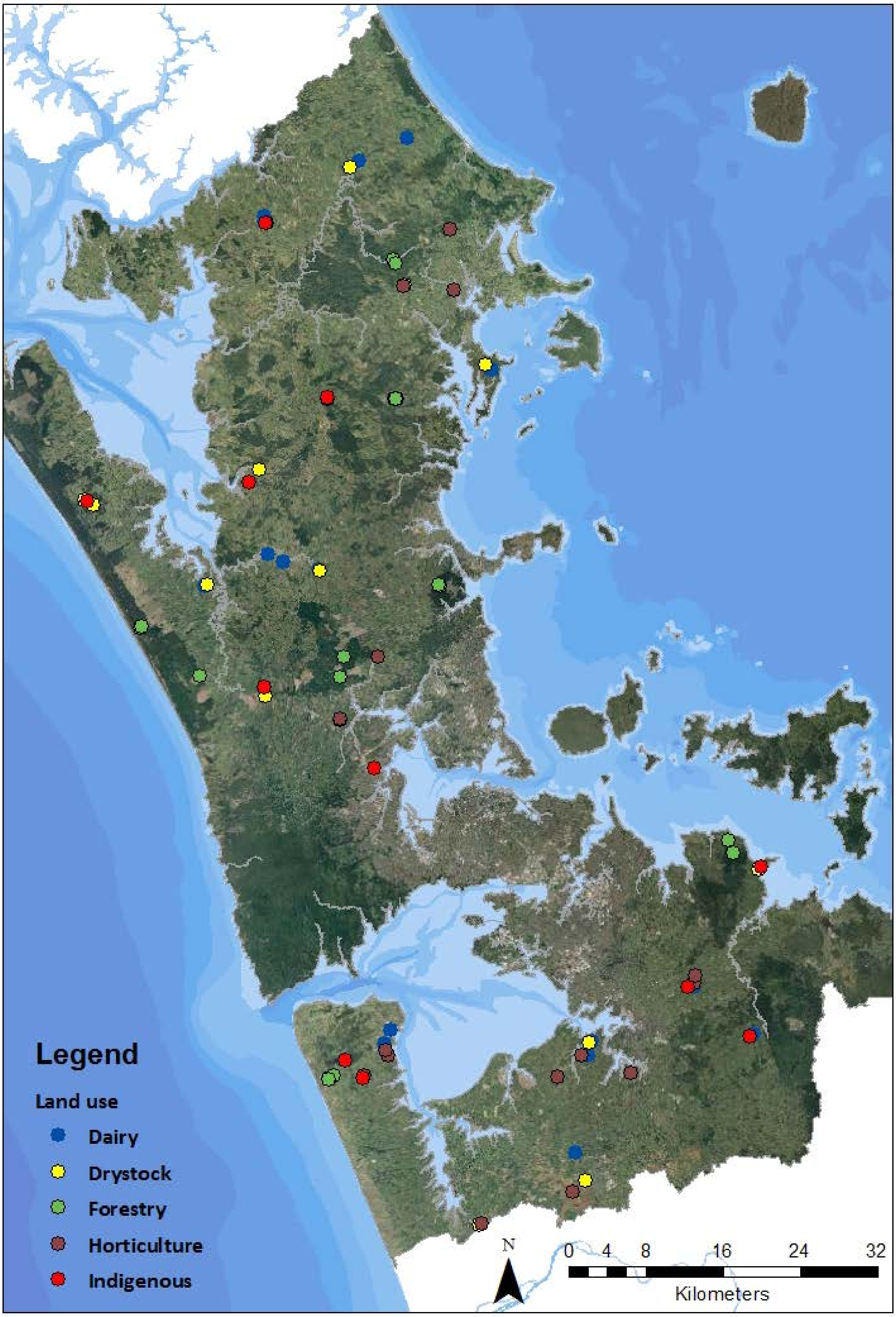

Figure 1. The distribution of the 84 soil sampling sites for trace element analyses within Auckland.

Note: As yet no sites have been selected on the Great Barrier Island.

2.2 Soil chemical analysis

Soil samples were air-dried and sieved to <2mm before chemical analysis. Total recoverable arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) were determined by digesting soil in nitric/hydrochloric acid and the trace elements were analysed in the digest by inductively coupled plasma mass spectrometry (USEPA 200.8). All analyses were carried out at IANZ-accredited laboratories (Watercare Laboratory Services). For some soil parameters, measurements were below the detection limits and a nominal value equalling half of the detection limit was assigned to these measurements.

2.3 Statistical analysis

Trace element concentrations were tested for normality and transformed if necessary before being subjected to ANOVA fitting terms for land use, Soil Order and sampling period (i.e. 1999-00 and 2008-11, hereafter referred to as pre and post 2000). Blocking was used when comparing between the two sampling periods and site number used as the blocking factor. Where used, the *F*-statistic is based on log scale data with corresponding back-transformed standard error of difference (SED) and least significant difference (LSD) values. Summary data for trace element concentrations for eight analytes are presented as box and whisker plots. The boxes represent the inter-quartile range (25th to 75th percentile) and the whiskers show the range of values that fall within the 10th and 90th percentile. Outliers are illustrated with black circles. The median and mean are shown as a straight and dashed line, respectively, in each box. All analyses were carried out using the statistical package Genstat 17th edition and graphics using Sigmaplot 12.0 edition.

3.0 Results and discussion

Concentrations for the eight trace elements are illustrated in Figure 2. Trace elements that exceeded recommended guidelines (with number of samples exceeding guidelines in parentheses) include arsenic (1), cadmium (4) and copper (1) (Figure 2 and Table 1). Although there are several outliers that fall outside the 10th and 90th percentiles, the majority of outliers are within the recommended guideline range for soil health (Table 2).

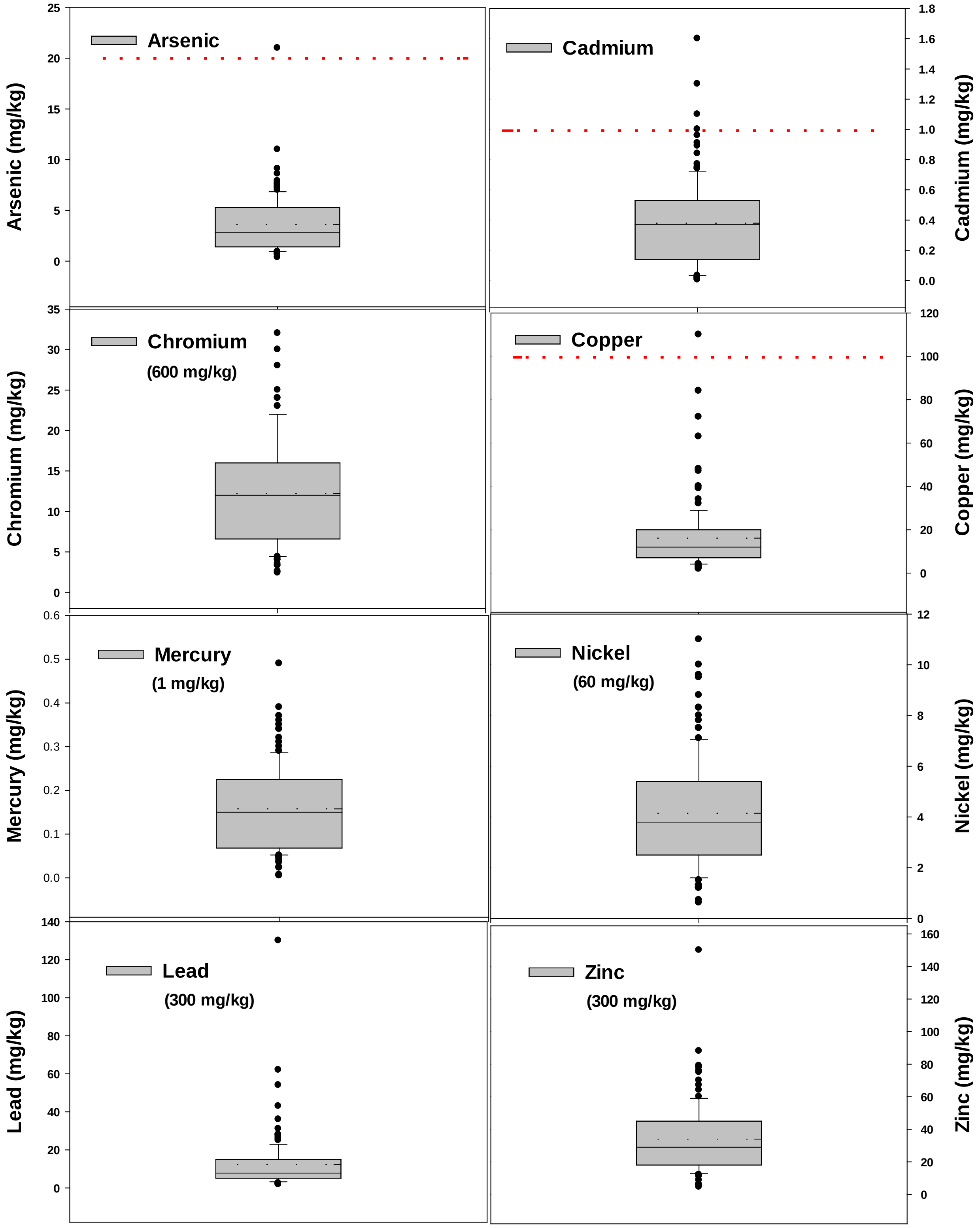

Figure 2. Trace element concentrations (mg/kg) at the soil quality monitoring sites. The dashed red lines illustrate upper limits for specific analytes and demonstrate where guidelines were exceeded and upper limits highlighted for remaining analytes (in parentheses).

3.1 Trace elements and land use

Toxicity of **arsenic** (As) can cause acute and chronic effects on soil biota and restrict photosynthesis and plant growth. Bioavailable forms of As are reported to be more detrimental than forms of total As (Cavanagh and O'Halloran, 2006). Major sources of As include geothermal springs, discharges from geothermal power stations and CCA (Copper-Chromium-Arsenic) treated timber (Robinson et al., 2004). Other sources of As include sheep dip sites that by law were on every sheep farm in New Zealand where organochlorines and As compounds were used to rid sheep of pests. As consequence, chemical residuals have the potential to remain in soil for decades or be transferred to surface or ground water posing a risk to both environmental and human health.

Only one soil sample exceeded As recommended guidelines (Table 1) which was first sampled in 2000 under drystock farming. When this site was re-sampled in 2010 concentrations of As fell within the guideline range. Considering that only two sampling periods have been carried out, it is difficult to ascertain if concentrations in As have truly decreased or whether it is the result of spatial variability or analytical uncertainty. Regarding trend analysis, the end goal is to be able to compare concentrations of trace elements across five sampling periods, which will provide us with more certainty about changes in these soil parameters over time. Mean concentrations of As were not significantly different for land use types (Table 2).

Table 1. Mean, minimum and maximum concentrations (mg/kg) of trace elements and number and percentage of trace elements exceeding guidelines for agricultural soils.

Element	Mean	Min	Max	Number of samples exceeding guideline	% Exceeding guideline
Arsenic (As)	3.61	0.36	21	1	1
Cadmium (Cd)	0.48	0.09	1.6	4	3
Chromium (Cr)	12.05	1.9	38	0	0
Copper (Cu)	16.55	2.2	110	1	1
Mercury (Hg)	0.21	0.04	0.72	0	0
Nickel (Ni)	4.38	0.63	17	0	0
Lead (Pb)	12.57	1.8	130	0	0
Zinc (Zn)	40.95	1	150	0	0

Four of the 123 individual soil samples analysed for **cadmium** (Cd) exceeded recommended guidelines (Table 1). These four samples represented two separate sites, a horticultural and dairy site. The former site was first sampled in 1999 and again in 2008 and the latter site in 1999 and again in 2009. Cadmium concentrations at both sites exceeded and continued to exceed the guideline range for soil health when first sampled before 2000 and when repeated in 2008/11. However, it is important to note that concentrations are presented on a gravimetric basis (mg/kg) which does not take into account the soil's bulk density at the site. Both these sites were located on an Ardmore peaty loam soil, classified as an Organic Soil Order following the New Zealand Soil Classification (Hewitt 1998), with an average recorded bulk density of 0.57 g/cm^3 for the four soil samples. Therefore, the true levels of Cd have been overestimated and on a volumetric basis, levels of Cd range from 0.59-0.99 g/m^3 for the same four soil samples. This highlights the importance of considering the inherent physical characteristics of soils otherwise presenting data on a gravimetric basis can sometimes over- or under-estimate the true levels of trace elements. It is also important to note that for Cd, soil guideline values that have been derived for food safety, ecological receptors, human health and groundwater have been derived using gravimetric values (Cavanagh et al., 2013); therefore the reporting of Cd levels using both sets of units will prove useful.

Table 2. Mean concentrations (mg/kg) of trace elements for five differing land uses and guideline (mg/kg)[1] and background (mg/kg)[2] upper limits for agricultural soils. The *F*-statistic, standard error of differences (SED) and least significant differences (LSD $_{05}$) are given for comparison between means of trace element concentrations and land uses.

Suggested upper limit	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
(mg/kg)[1]	**20**	**1**	**600**	**100**	**1**	**60**	**300**	**300**
Dairy	3.32	0.59	13	16	0.21	5.0	15	43
Drystock	4.25	0.38	12	11	0.18	3.9	13	32
Forestry	4.44	0.07	11	10	0.05	3.7	6	21
Horticulture	2.97	0.45	13	27	0.16	3.7	12	34
Indigenous	3.31	0.11	12	10	0.15	4.4	16	36
***F*-statistic**	ns	*P*<0.001	ns	*P*<0.001	*P*<0.001	*P*<0.05	*P*<0.001	*P*<0.001
SED	0.691	*0.074*	1.8	*2.7*	*0.026*	*0.58*	*2.3*	*4.9*
LSD$_{05}$	1.375	*0.148*	3.6	*5.5*	*0.051*	*1.14*	*4.5*	*9.8*
ARC 2001 (mg/kg)[2]	12	0.65	55-125*	45-90*	0.45	35-325*	65	180-1160*

[1]Recommended soil upper limits for eight trace elements in agricultural soils. New Zealand Water and Wastes Association, 2003.
[2] Upper background concentrations of trace elements in Auckland soils (ARC 2001)
* Lower range is the upper threshold for non-volcanic soils and the upper range is the upper threshold for volcanic soils

Mean concentrations of Cd across 123 soil samples in the current study were calculated to be 0.38 mg/kg (0.005-1.6 mg/kg) (Figure 2) and concentrations were significantly different for land use types (Table 2). Mean Cd concentrations were greatest for dairy sites followed by horticultural sites. High concentrations of Cd for more intensive land uses are not uncommon as phosphorus fertiliser is a major source of Cd in soils (Roberts et al., 1994). For example, superphosphate fertiliser application has been reported to be the cause of increased Cd concentrations and after 60-70 years of historic fertiliser use, farmed soils were reported to be on average six times that of background soils (Taylor et al., 2010). Applications of phosphate fertiliser was also reported to be the cause of elevated Cd concentrations (range <0.1 to 1.5 mg/kg) from the Auckland, Tasman and Waikato regions (Gaw et al., 2006).

Gray (2011) reported that trace element concentrations were comparable for vineyards, cropping, pasture, dairy, native bush and exotic forest at the 0-10cm soil depth, except for Cd for four contrasting soil types in Marlborough. Concentrations of Cd were greater on dairy farms which have previously been related to surface applications of phosphate fertiliser to maintain production (Longhurst et al., 2004). Similarly, when farmed soils were compared with non-farmed (native bush, reserves, parks, or waste areas) comparable soils, Roberts *et al.* (1994) reported significant enrichment of Cd (0-7.5 cm depth) in five out of the eight soil groups on farmed sites (0.44 mg/kg) over background non-farmed soils (0.2 mg/kg). The elevated Cd concentrations for pastoral soils were attributed to P fertiliser applications on such soils. Environment Canterbury (2006) also reported that concentrations of Cd were greater for regional than that of urban soils. Furthermore, Roberts *et al.* (1994) reported that concentrations of Cd were generally greater at the 0-2.5 cm depth and lower at the 2.5-7.5 cm sampling depth. The difference in Cd concentrations with depth was attributed to a 'dilution' factor with depth where it does not receive direct surface application of Cd through fertiliser application, herbage recycling through stock defecation, and the crushing and burial of pasture by grazing stock; all of which are functions of soil management. For example, Taylor *et al.* (2007) reported that concentrations of Cd under cropping were less than that for pastoral land use because of frequent ploughing to a 20 cm soil depth that allowed dilution of Cd concentration. The dilution effect will also be apparent after pasture renewal for pastoral grazed systems.

Taylor *et al.* (2007) reported 0.35 mg/kg as a national average concentration for Cd (range between 0-2.52 mg/kg) and New Zealand Water and Wastes Association (2003) suggested the upper concentration limit of 1.0 mg Cd/kg to meet a number of requirements which can include the protection of human, plant and animal health, groundwater quality and soil environmental values (Table 2). Furthermore, the National Cadmium Management Strategy that underwent international review (MAF, 2011) provides a national approach for managing Cd in New Zealand. The Tiered Fertiliser Management System (TFMS) is a pivotal component of the strategy and aims to manage

Cd accumulation in soil through the practice of stringent phosphate fertiliser management practices. There are five tiers and four trigger values, based on increasing soil Cd concentrations, which result in different levels of action primarily related to phosphate fertiliser application (Table 3). The document is considered to be of higher level than the limits reported by the NZWWA (2003).

Table 3. Required management actions in relation to specified cadmium (Cd) concentrations trigger values, and the source of the trigger value (Cavanagh, 2012, MAF, 2011)

Tier	Management action	Cd concentration (mg/kg)	Trigger value (mg/kg)	Source of value
0	Five-yearly testing	0–0.6	0.6	99th percentile of natural
1	Application is restricted to a set of products and application rates to minimise accumulation, and 5-yearly testing	>0.6–1.0	1.0	NZ Biosolids guidelines (NZWWA 2003)
2	Application rates are further managed by use of a cadmium balance programme to ensure that Cd does not exceed an acceptable threshold within the next 50 years	>1.0–1.4	1.4	Canadian SQG (human and ecological) for agricultural land use (CCME, 1999)
3	Application rates are further managed by use of a Cd balance programme	>1.4–1.8	1.8	UK Soil Guideline value for allotments (EA, 2009)
4	No further accumulation above the trigger value	>1.8		

This upper limit for Cd was exceeded for several horticultural, drystock and dairy sites, and one urban site for soils across the Waikato region (Taylor *et al.* 2010). The presence of elevated Cd is of greater concern in New Zealand when compared to agricultural soils overseas because the pH of New Zealand soils tends to be in the lower acidic range that allows greater plant uptake of the element (Kim and Taylor, 2009) and as thus can potentially enter the food chain. For example, the average pH of soil under native bush in Auckland has been measured at 5.4 versus 5.9 under rural land use activities (Curran-Cournane, 2015). Taranaki Regional Council (2005) reported mean Cd concentrations to be less than half the current 1.0 mg Cd/kg limit and it was estimated to take over 265 years before the average concentration of Cd in soil would exceed the upper Cd limit, however this would largely be dependent on P fertiliser inputs (Longhurst, 2006). The National Cadmium Group reported that neither a voluntary industry level on Cd content in fertiliser, nor the weighted average cadmium contents achieved were adequately low enough to prevent Cd accumulation in agricultural soils as a result of phosphate fertiliser use (MAF, 2008). An attempt was made to estimate a national Cd historic accumulation rate but was hindered by lack of historical fertiliser information (Taylor et al., 2007).

One soil sample exceeded recommended guidelines for **copper** (Cu) (Table 1) which was located on an apple orchard site in 2008. In 2000 concentrations of Cu at this site were also recorded to be high at 72 mg/kg. The soil type at the site was classified as a Typic Orthic Gley with a recorded bulk density of 1.25 g/cm^3, therefore, the gravimetric levels have underestimated the true levels of Cu at the site (i.e. 110 mg/kg vs 138 g/m^3). Future monitoring will be important to determine if concentrations continue to increase into the future. For now, this information can be used to inform land managers about where and what land management advise should be provided to certain rural landowners.

Copper is an essential trace element for plant and animal growth and negative effects can result from either copper deficiency or surplus. In New Zealand, soils that are more susceptible to Cu deficiencies include Organic and Podzols Soil Orders and strongly leached sandy soils (McLaren and Cameron, 1996). Unlike most trace elements, Cu has limited mobility in soil as it strongly absorbs to some soil particles (Cavanagh and O'Halloran, 2006). Significant differences in concentrations of Cu existed for land use with concentrations being greatest for horticulture (27 mg/kg) and Gley (32 mg/kg) soils, respectively (Tables 2 and 3). However, only 7 sites (14 soil samples) were classified as being Gley soils therefore concentrations of Cu were largely influenced by land management.

Gaw (2002) reported that Cu frequently exceeded baseline levels for soils in cropping areas in the Auckland region and some levels exceeded guidelines recommended for the protection of human health. Similarly, Cu was frequently exceeding recommended guidelines in horticultural soils from the Tasman, Waikato and Auckland regions and concentrations were greater than those detected in grazed soils (Gaw et al., 2006). Excessive concentrations of Cu were attributed to the long term spraying of copper-based fungicide, agrichemicals and fertilisers (Gaw et al., 2006). These authors reported that concentrations of Cu were greatest for orchards followed by vineyards and market gardening sites and mean concentrations in orchards were 224 mg/kg (range 21-490 mg/kg). In the current report, the majority of horticultural sites were orchard sites (10 of the 18 sites from at least the mid-1990s), yet mean concentrations of Cu for horticulture was 27 mg/kg, well within the recommended guideline range (Table 2). This is not necessarily attributable to policy or land management effectiveness as the locations of sites will be different across both studies.

Several regional councils have also reported concentrations outside the upper limits for such elements but mean and median concentrations always fell within the specified guidelines for various land uses. For example, Cd concentrations for dairy pasture and Cu and Cd concentrations for kiwifruit orchards were the analytes that most frequently exceeded upper limits during 2009-10 sampling events in the Bay of Plenty (Guinto, 2011). While, mean concentrations for these analytes were within the recommended guideline range, it is still important to note and monitor exceedances that arise at individual sites. In 2009-10, Sorensen (2010) reported that mean trace element concentrations did not exceed any of the guidelines for market garden and cropping sites in the Wellington region but for dairy sites, in 2008-09, two sites exceeded Cd and As concentrations (Sorensen 2009). It will be important to continue revisiting sites that currently exceed soil guidelines to ensure concentrations do not increase.

Concentrations of **chromium** (Cr), **mercury** (Hg), **nickel** (Ni), **lead** (Pb) and **zinc** (Zn) did not exceed guidelines for any given soil sample. Significant differences in mean concentrations of trace elements were observed across land uses in the current study except for As and Cr (Table 2). Chromium (Cr) is not essential for plant growth and high concentrations of Cr have been associated with soils of volcanic mineralogy, particularly for basalts (ARC 2001). Gray (2011) reported high concentrations of Cr (range 110-178 mg/kg) for dairy farm sites in the Marlborough region and attributed this to the possible serpentine minerals contained within the soil parent rock. The influence of parent material on trace element concentrations was not explored in the current report.

In the current study, while concentrations of Cd and Cu were higher for the more intensive dairy and horticulture land uses, respectively, concentrations of Hg, Ni and Zn were also highest for dairy sites, perhaps also related to the intensive nature of the land use. Sources of Zn in rural areas include the use of facial eczema remedies (pastoral land) and pesticides (horticultural land) (Cavanagh and O'Halloran 2006; Kim and Taylor 2009; Longhurst *et al.* 2004). However, concentrations of Zn tend to be greater in urban areas than for rural areas and sources in urban areas include zinc-coated metal roofs and the wearing of car tyres (Councell et al., 2004). These authors estimated that in 1999 the quantity of Zn released by the wearing of tyre in the United States of America was between 10,000-11,000 metric tonnes. Environment Canterbury (2006) also reported that soil samples collected within the urban area tended to have greater trace element concentrations than soils collected in the rural area and that this was associated with urban pollution. Urban sites were not the focus of the current report and is an information gap worth filling for the largest city in New Zealand. Green spaces in the urban environment provide aesthetic and recreational values, they mitigate flooding and regulate greenhouse gas emissions. What's more, vegetable gardens are becoming increasingly common amongst residential households and soil sampling will provide an indication of soil health for such activities within the urban environment that could ultimately affect human health via consumption.

While concentrations of Cd, Cu, Hg, Ni, Pb and Zn were significantly different across land uses, mean levels were all within recommended guideline ranges and no significant differences in changes were observed across sampling period except for Ni at the $P<0.05$ level (Table 4) which will be discussed further below. It is noteworthy that exceedances did arise at six individual sites and this highlights the importance of future monitoring particularly at these sites. Furthermore, only data for 11 native bush sites were reported in the current study and therefore additional information on trace element concentrations under this land use, i.e. uninfluenced by anthropogenic activity, would be very useful to inform better background conditions.

3.2 Trace elements and Soil Order

Significant differences were observed for mean concentrations of all trace elements and Soil Order (Table 3). This is not surprising given that the classification of soils is related to their physical and chemical characteristics which are, in turn, a function of the evolution (weathering processes/climate) from the parent material (mineralogy) (Hewitt, 1993). Furthermore, the mobility of trace elements has not only been reported to be pH dependent but also to be Soil Order dependent (ECan 2006; Kim and Taylor 2009).

Table 3. Concentrations (mg/kg) of trace elements for seven contrasting Soil Orders.

Element	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Allophanic	5.71	0.58	15	15	0.21	5.4	18	46
Brown	3.79	0.19	11	12	0.12	4.1	11	36
Gley	2.65	0.41	6	32	0.16	3.2	7	24
Granular	4.40	0.43	16	16	0.21	4.8	26	44
Organic	2.56	0.84	16	24	0.21	5.2	15	47
Recent	5.06	0.12	9	10	0.12	3.9	4	25
Ultic	1.63	0.24	11	12	0.11	3.0	5	22
***F*-statistic**[1]	$P<0.001$	$P<0.001$	$P<0.001$	$P<0.001$	$P<0.001$	$P<0.01$	$P<0.001$	$P<0.001$
SED	*0.63*	*0.093*	*1.7*	*3.0*	*0.031*	*0.60*	*1.7*	*5.1*
LSD_{05}	*1.26*	*0.185*	*3.3*	*5.9*	*0.061*	*1.19*	*3.4*	*10.0*

In contrast to many studies focusing on land use relationships with regard to trace element concentrations, relationships between soil type or order and trace elements are not analysed and appear only in appendices (Gray 2011; Guinto 2011). The fertiliser signature and copper-based fungicides can sometimes overwhelm what is naturally present in the parent material for Cd and Cu, respectively (Gaw 2002; Taylor *et al.* 2007), and the same can be said for applications that are typical of other land uses. This, therefore, reinforces the importance of carrying out additional sampling for native bush sites to capture those naturally occurring background concentrations in soils.

Furthermore, and as previously discussed, it is also important to consider the bulk density of the soil when comparing trace elements across differing Soil Orders. For example, levels of trace elements will be very different for soils that are relatively heavy and dense versus those that are light and peaty (Taylor *et al.* 2007). Therefore, when comparing levels of trace elements across Soil Orders comparisons should be conducted using volumetric data. The output of which will allow better data gathering of trace elements for Soil Orders for regional councils to be used for national reporting which can also be used to set upper limits. However, and similarly to the Cd situation, the majority of guideline values for food safety, ecological receptors (Cavanagh and McNeil, 2015), human health (MfE, 2014) and groundwater have been derived using gravimetric values, therefore the reporting of trace elements using both sets of units will prove useful.

3.3 Changes in concentrations of trace elements

There were no significant differences between trace element concentrations in the 39 repeat sites that were sampled pre and post 2000, except for Ni at the $P<0.05$ level (Table 4). Concentrations of Ni increased from 3.6 to 4.1 mg/kg pre and post 2000, respectively. Mean concentrations of Ni were within the ceiling limit of 60 mg/kg and within the upper limit of background conditions for non-volcanic soils (i.e. < 35m/kg) for all soil samples (Figure 2) so no cause for concern is currently warranted. However, it will be important to monitor concentrations of trace elements, especially Ni, for multiple sampling periods to determine if increases occur over time.

Furthermore, and as previously discussed, caution is recommended when only two sampling periods are being used to determine changes in concentrations of trace elements. The overarching goal is to be able to compare concentrations of trace elements over time for trend analysis using five sampling periods. While the comparison of two sampling periods does provide a useful starting point, as monitoring continues the use of a longer spanning data record will allow more confident identification of where soil problems exist and where resources need to be targeted.

Table 4. Mean changes in trace element concentrations pre and post 2000 sampling in the Auckland region

Sampling period	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Pre 2000	3.73	0.44	11	16	0.15	3.6	11	30
Post 2000	3.65	0.47	12	17	0.18	4.1	12	35
***F*-statistic**	ns	ns	ns	ns	ns	$P<0.05$	ns	ns
SED	0.264	0.021	0.6	1.0	0.022	0.21	0.7	1.9
LSD_{05}	0.535	0.042	1.3	1.9	0.045	0.43	1.4	3.9

4.0 Conclusions, recommendations and future research

Although, all trace element mean concentrations did not exceed recommended guidelines for environmental soil health, six soil samples exceeded the guideline range (with number of samples in parentheses) which included arsenic (1), cadmium (4) and copper (1) and future monitoring will be important at these sites. These findings were comparable to those reported by other regional councils for rural soils in New Zealand.

Concentrations of trace elements were significantly different for land use and Soil Orders. There were no significant differences between mean trace element concentrations in the 39 repeat sites that were sampled pre and post 2000, except for an increase in nickel.

Recommendations include the following:

- Re-sampling indigenous sites, as well as selecting new indigenous sites to sample, in order to statistically calculate up-to-date natural background concentrations and to identify natural and spatial variations.

- Assessing and quantifying concentrations of trace elements in urban Auckland to determine how anthropogenic and industrial impacts might affect soil functional health within this urban setting.

- Consider determining levels of trace element with the incorporation of bulk density for each site to correct for any over- and under-estimation of the true levels.

- Lastly, all productive sites should be re-sampled every five years to identify changes in trace element concentrations between sites, especially those sites that currently exceed guidelines, and to establish trends. For sites that consistently exceed guidelines, land managers should advise and provide a suite of best management practices or develop a personal farm management plan for land owners to ensure the management of soil health. If trace element concentrations continue to increase at these sites, a more detailed soil-sampling regime should be undertaken to determine if the site should be treated as contaminated.

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