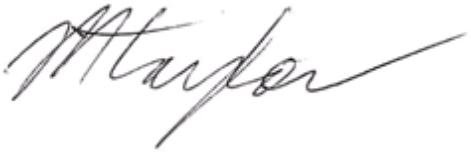
Concentrations of Selected Trace Elements for Various Land Uses and Soil Orders within Rural Auckland

Auckland Council
Technical Report 2012/021
ISSN 2230-4525 (Print)
ISSN 2230-4533 (Online)

ISBN 978-1-927169-34-6 (Print)
ISBN 978-1-927169-35-3 (Online)

Reviewed by:



Name: Matthew Taylor

Position: Soil Scientist

Organisation: Waikato Regional Council

Date: 18/07/12

Approved for
Auckland Council publication by:

Name: Grant Barnes

Position: Manager Research Investigations and Monitoring Unit

Organisation: Auckland Council

Date: 18/07/12

Recommended citation:
Curran-Cournane F. and Taylor A. (2012). Concentrations of selected trace elements for various land uses and Soil Orders within rural Auckland. Prepared by Auckland Council and Waikato Regional Council. Auckland Council Technical Report 2012/021

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

Dr Fiona Curran-Cournane (Auckland Council)
Amy Taylor (Waikato Regional Council)

Contents

Executive summary

Trace elements are naturally present in soils that are inherited from the parent material of the underlying rock as well as occurring naturally as a result of 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 this can have adverse effects on soil, plant and animal health. Trace elements can ultimately enter the food chain and/or be ingested in dust resulting in human health impacts.

Soils were sampled from 84 sites across the Auckland Region between periods 1999-00 and 2008-11 and 39 of the sites that were sampled between 1999-00 were repeated between periods 2008-11, a total of 123 soil samples from 84 sites. Samples were composites of 25 cores. These 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 use activities. The sites selected represented seven Soil Orders namely Allophanic (12), Brown (19), Gley (7), Granular (13), Organic (7), Recent (4) and Ultic (22). Each composite soil sample was analysed for total recoverable arsenic, cadmium, copper, chromium, mercury, nickel, lead and zinc.

All trace element mean concentrations did not exceed recommended guidelines for environmental soil health. However, on an individual basis nine soil samples exceeded the guideline range which included (with number of samples in parentheses) arsenic (1), cadmium (4) and copper (4). These nine soil samples represent five sites. The site that exceeded arsenic guidelines was first sampled in 2000 and when repeated in 2010 fell within the guideline range for soil health. In contrast, the remaining four sites that exceeded Cd and Cu concentrations for soil health exceeded and continued to exceed the guideline range when first sampled in 1999-00 and when repeated in 2008-11. These elevated trace element concentrations can threaten the life-supporting capacity of soil at these sites.

Concentrations of trace elements were also significantly different for land use and Soil Orders.

Recommendations include the following:

- Focusing on re-sampling indigenous sites to provide up to date background concentrations for trace elements. Future research should also focus on characterising the parent mineralogy of the underlying rock to further ascribe background trace element concentrations

- Assessing and quantifying the concentrations of trace elements in urban Auckland to determine how anthropogenic and industrial impacts might affect soil functional health within the urban environment. Green areas in the urban environment provide many services such as aesthetic and recreational values. Furthermore, 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 through consumption

- Determining trace element concentrations with soil depth to determine if or how atmospheric transfer and deposition influence concentrations in urban Auckland

- Lastly, all 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 to 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.

1.0 Introduction

Trace elements are naturally present in the environment and in soils they are inherited from the parent material amongst other sources. Soils with similar parent material typically have similar concentrations of trace elements and concentrations 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 zinc and copper 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 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 eg, Longhurst *et al.* 2004; 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 eg, Auckland Regional Council (ARC 2001), Marlborough District Council (Gray 2011), Environment Canterbury (ECan 2006) and, the then, Environment Waikato (Kim and Taylor 2009). Not all trace elements are essential for plant health and animal growth. Nonessential 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 that looked at trace element concentrations in horticultural soils in Auckland soils in 2006, 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 element concentrations for various land uses and Soil Orders in rural Auckland.

2.0 Materials and methods

2.1 Sample sites and soil sampling

The total number of sites chosen for a suite of trace element analysis in a variety of land use and Soil Orders was 84, which 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 in the 2008-11 sampling events and the data reported is on a combination of 123 homogeneous soil samples. These sites have also been used for the national '500 Soils Programme' that was initiated in 1995 whereby 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 regions land use 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 annual cropping, market garden vegetable production and orchards. The Soil Orders were identified as Allophanic (12 sites), Brown (19), Gley (7), Granular (13), Organic (7), Recent (4) 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 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.

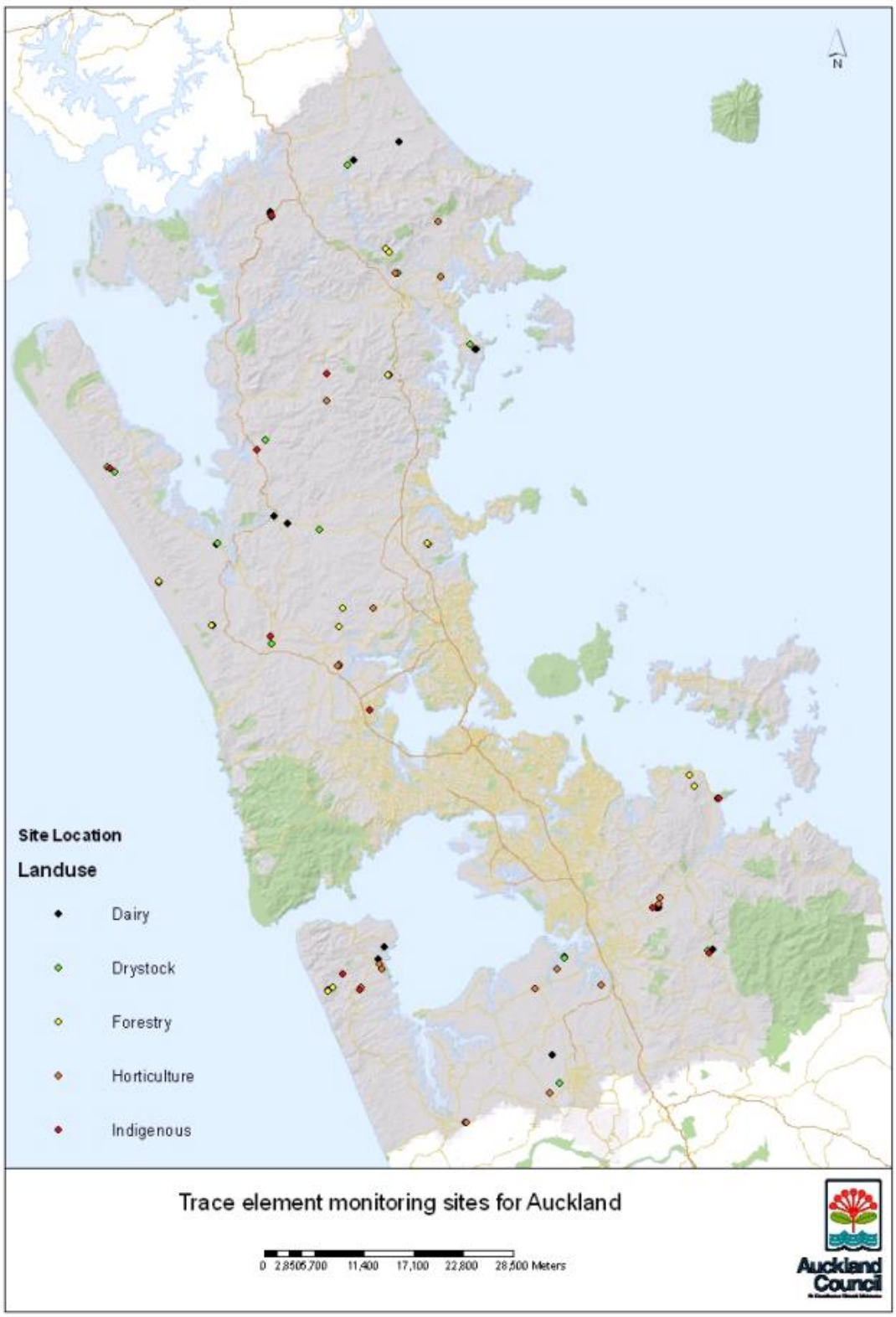


Figure 1. The distribution of the 84 soil sampling sites for trace element analyses within Auckland.

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 copper, chromium, cadmium, arsenic, lead, nickel and zinc 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.)

2.3 Statistical analysis

Trace element concentrations for land use and Soil Order were tested for normality and transformed if necessary before being subjected to ANOVA and to determine changes in trace elements for repeat sites sampled before and after 2000. Summary data for trace element concentrations for eight analytes are presented as Box and Whisker plots. All analyses were carried out using the statistical package Genstat 14 (GenStat 2011) and graphics using Sigmaplot 12 (SigmaPlot 2011).

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 (4) (Figure 2 and Table 1). Although there are several outliers that fall outside the 5th and 95th percentiles, the majority of outliers are within the recommended guideline range for soil health (Table 2).

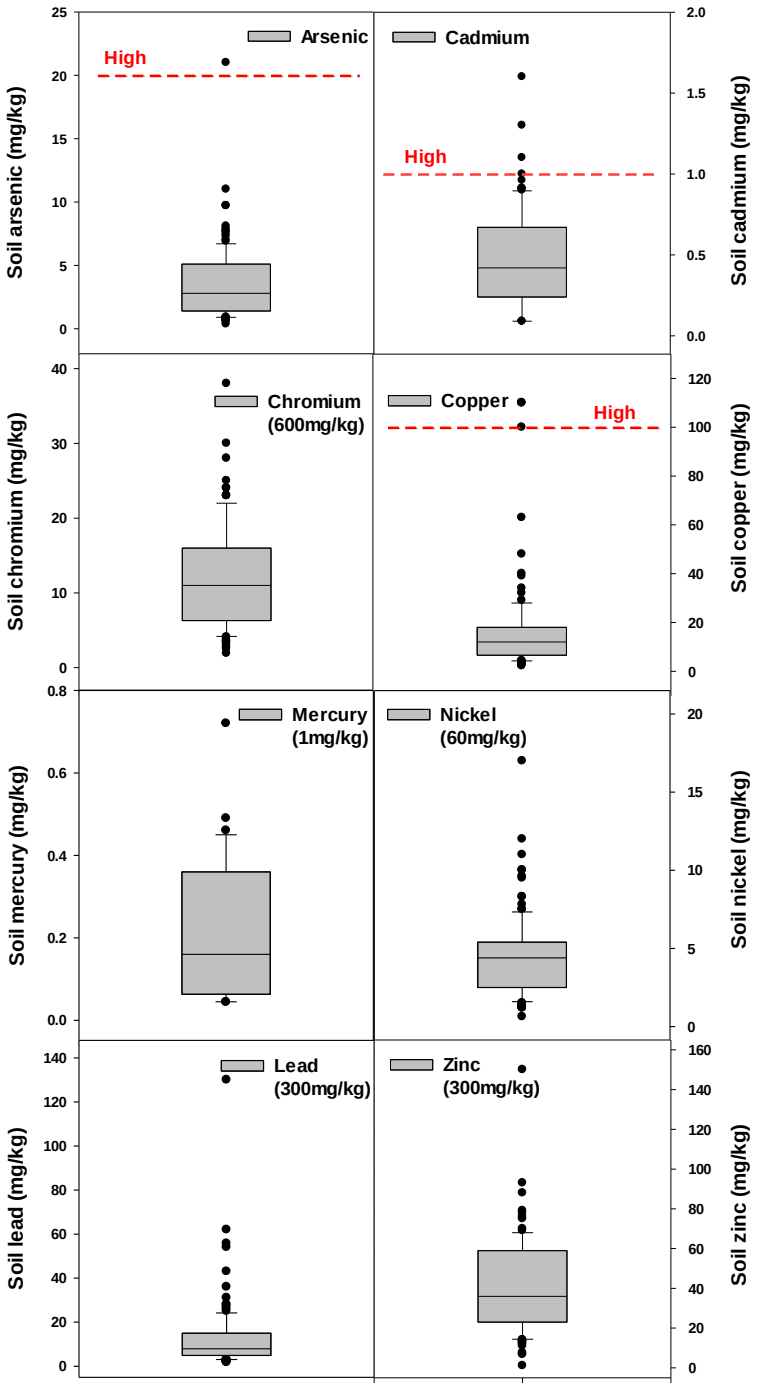


Figure 2. Trace element concentrations (mg/kg) at the soil quality monitoring sites. The dashed red lines illustrate upper limits for specific analytes and demonstrate where guidelines were exceeded and upper limits highlighted for remaining analytes (in parentheses). The boxes represent the inter-quartile range (25th to 75th percentile) and the whiskers show the range of values that fall within the inner fences. Outliers are illustrated with black circles. The median is shown as a line in each box.

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). Concentrations of As in lakes and rivers in the Taupo Volcanic Zone exceed drinking water guidelines (0.01 mg/L- World Health Organisation) and major sources 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 whereby 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. Currently, there is ongoing research investigating the applicability of biochar to enhance the solubility of As to encourage arsenic plant uptake (Gregory *et al.* 2011). However, enhancing solubility is likely to enhance leaching as well as plant uptake.

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. Concentrations of As were not significantly different for land use types but were for Soil Orders (Tables 2 and 3) with concentrations being greatest for the better structured Allophanic and Brown Soil Orders and least for poorly structured and heavy Ultic and Recent Soil Orders.

Table 1. Mean, minimum and maximum concentrations 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	4	3
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 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. Both these sites are located in the former Papakura district on Ardmore peaty loam soil classified as an Organic Soil Order following the New Zealand Soil Classification (Hewitt 1998). Organic soils had significantly greater concentrations of cadmium (Cd) for all Soil Orders and, amongst other variables, the mobility of Cd has been reported to be organic matter content, dependent (Cavanagh and O'Halloran 2006). Olsen P concentrations for these two sites across the four sampling years were high (range 52-78 mg/kg, data not shown) which is another factor that explains high Cd concentrations for this Soil Order. Superphosphate fertiliser application has been reported to be the cause of increased Cd concentrations and after 60-70 year 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).

Concentrations of Cd were also significantly different for land use types (Table 2), with forestry and dairy sites having greatest concentrations of cadmium. High Cd concentrations at forest sites were not expected and were not reported to be of concern in Waikato (Taylor 2012; Taylor *et al.* 2010). Mean Olsen P concentrations for 15 plantation forest sites sampled in 2011 reported in the current study was 20 mg/kg (range 4-68 mg/kg) (Curran-Cournane 2012). Following a more recent workshop reviewing soil quality indicators, in May 2011 (Taylor 2011), recommended guidelines for Olsen P in plantation forests was revised as 5-30 mg/kg. Of the 15 plantation forestry sites sampled in 2011, four sites exceeded the guideline and only one site would be considered to have severely exceeded the guideline at 68 mg/kg. Although mean Olsen P concentrations were below the recommended upper limit for soil health large historic applications of P, when this land was in other land uses, could be associated with high remnant Cd concentrations (Matthew Taylor, pers. comm.). The mean Zn:Cd ratio for the 15 forestry sites was 72. Fertilised sites tend to have Zn:Cd ratios around 100 whereas unfertilized sites have Zn:Cd ratios of >120. Zinc concentrations at these sampled sites were reasonably low (mean 61 mg/kg) overestimating the influence fertiliser application would have played. However, sources of Cd are not only anthropogenic in origin but can also occur geologically from parent rock with sedimentary rocks reported to have Cd concentrations at the higher end (Cook and Freney 1988). This could provide an alternative explanation in that high Cd concentrations at these sites could be associated with the parent material of these soils whereby interfaceous or volcanic material have characteristically high P retentive properties (Molloy 1993). This would require further

investigation. Furthermore, although indigenous sites were reported in the current report, these sites were last sampled between 1999-00 and future sampling should concentrate on revisiting these sites to update background Cd concentrations and determine if this is interfaceous-associated material and whether it has an effect on Cd concentrations.

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 (Recent, Granular, Gley, Organic, Ultic, Allophanic, Pumice and Pallic) 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 fertiliser P applications on such soils. Environment Canterbury (2006) also reported that concentrations of Cd were greater for regional than urban Gley, Saline Gley Recent and Organic Soil Orders. 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 or herbage recycling through stock defecation and the crushing and burial of pasture by grazing stock all of which is a function 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 allows dilution of Cd concentration.

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). 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 can potentially enter the food chain. 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 in soil, however this would largely be dependent on the fertiliser P 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 are 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).

Table 2. Mean concentrations (mg/kg) of trace elements for five differing land uses and guideline (mg/kg)[1] and background (mg/kg)[3] upper limits for agricultural soils. The *F*-statistic is 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	13.13	16	0.2	5.54	14.7	43.1
Drystock	4.26	0.38	11.83	10.5	0.27	3.94	12.7	37.5
Forestry	4.35	0.67	9.04	6.9	0.33	4.12	5.2	54.7
Horticulture	2.95	0.45	12.89	31.0	0.13	3.55	13.8	33.3
Indigenous	3.32	0.14	12.51	10.1	0.11	4.83	15.8	40.2
F-statistic[2]	ns	*P*<0.001	ns	*P*<0.001	*P*<0.01	*P*<0.05	*P*<0.001	ns
ARC 2001 (mg/kg)[3]	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] *F*-statistic based on log scale
[3] 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

Four soil samples exceeded recommended guidelines for copper (Table 1) and similarly to cadmium, these four samples represented two separate sites, both being horticultural sites on the same property but in adjacent paddocks (one paddock was an orchard for grapes and the other for apples). The soil was classified as a Typic Orthic Gley. Copper concentrations at both sites exceeded and continued to exceed the guideline range for soil health when first sampled in 2000 and when repeated in 2008. Copper (Cu) 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 by strongly adsorbing to soil particles (Cavanagh and O'Halloran 2006). Significant differences in concentrations of Cu existed for land use and Soil Order with concentrations being greatest for horticulture and Gley soils, respectively (Tables 2 and 3). Gaw (2002) reported that Cu frequently exceeded baseline levels for soils in cropping areas in the Auckland region and some levels exceeded guidelines 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 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), yet mean concentrations for Cu for horticulture was 31 mg/kg, well within the recommended guideline range.

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). However, mean concentrations for these analytes were within the recommended guideline range. 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.

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	14.84	15.2	0.22	5.37	17.7	45.9
Brown	4.84	0.36	8.85	8.2	0.21	3.88	7.0	45.4
Gley	2.62	0.40	6.20	39.7	0.14	3.84	6.6	23.2
Granular	4.56	0.44	16.82	16.0	0.25	5.32	27	46.3
Organic	2.55	0.84	16.48	24.1	0.21	5.23	15.3	47.5
Recent	1.49	0.36	13.88	27.5	0.24	4.62	7.8	42.2
Ultic	1.59	0.45	10.78	9.8	0.21	3.44	7.1	35.9
F-statistic[1]	*P*<0.001	*P*<0.001	*P*<0.001	*P*<0.001	*P*<0.05	*P*<0.05	*P*<0.001	*P*<0.01

[1] *F*-statistic based on log scale

Concentrations of chromium, mercury, nickel, lead and zinc did not exceed guidelines for any given soil sample. 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.

Concentrations of zinc (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 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).

Concentrations of mercury were greatest ($P<0.01$) and lead least ($P<0.001$) for forestry sites. Concentrations of mercury (Hg) and lead (Pb) have been reported to increase annually by about 0.5% and 0.2%, respectively, in the surface layer of forest soils in Sweden (Johansson *et al.* 2001). The increase in these trace elements was attributed to the impacts of atmospheric long-range transport and associated deposition, which could be an explanation for the increase in Hg levels in the forestry sites in the current report. However, heavy industry is not as common in New Zealand as it is in Europe and another possible explanation could be associated with forests having lower soil temperatures than that in pastoral based systems, with volatilisation being less with associated decreased soil temperatures (Matthew Taylor, pers. comm.). However, indigenous forests would also experience lower temperatures and concentrations of Hg were least at these sites and therefore high Hg concentrations at these forest sites could be associated with anthropogenic activity such as historic fertiliser application. Mercury was a common contaminant of sulphuric acid used to acidify phosphate rock to produce superphosphate which could be a possible source of Hg at these sites and, given the lower soil temperatures associated with forestry, Hg concentrations remain high with lower volatilisation (Matthew Taylor, pers. comm.). This explanation would need to be backed up with historic land use management at these sites which can be difficult to attain when it was up to 12years since some of these sites were last sampled and forest managers have since changed hands. However, Zheng *et al.* (2008) reported that long term P fertiliser application could potentially influence soil Hg concentrations but that Hg concentrations were more likely to be overwhelmed by the soil parent material. This would require further investigation which would be imperative if Hg concentrations met or exceeded the upper limit for soil health but which are currently not of concern. Furthermore, future sampling should also concentrate on revisiting indigenous sites to update

background trace element concentrations to determine what would be expected of undisturbed forest sites.

3.2 Trace elements and Soil Order

Significant differences were observed for all trace element concentrations and Soil Order (Table 3) and 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). Concentrations of Pb and Hg were significantly greater for Granular soils. Lead is not an essential trace element and it can have detrimental impacts on plants at concentrations of 100-1000 mg/kg. This study showed that only one sample from a non-intensive pastoral site sampled in 2009 had Pb concentrations (130 mg/kg) within this range which was located on a Granular soil. Granular soils represent nearly 20% of the soils within the Auckland Region and therefore a dominant Soil Order (NZLRI 2010). When this value was excluded from the dataset, significant differences remained apparent between Soil Order and Pb, with Granular soils having greatest concentrations. It is unclear why this Soil Order has significantly higher Pb and Hg concentrations and there is currently no information to compare these trace element concentrations with for this Soil Order. That said, concentrations of Pb and Hg for Granular soils in the current study were well within recommended target ranges for soil health and is not a cause of concern. It will be important to repeat the sampling of trace elements at these sites over time to determine if higher concentrations of Pb and Hg continue to be associated and are a genuine characteristic of Granular soils. Trace element deficiencies can also be Soil Order dependent. Kim and Taylor (2009) reported Pallic soils being particularly vulnerable to selenium, molybdenum and copper deficiencies and that Pumice soils were more susceptible to selenium, copper and cobalt deficiencies. Environment Canterbury (2006) reported that Gley urban soils had significantly greater concentrations of nickel, lead and zinc and Recent urban soils had greater concentrations of lead. In contrast, Gley soils in the current study had the lowest concentrations of lead and zinc and levels of nickel and lead were at the lower end for Gley and Recent soils, respectively. It is uncertain as to the reasons for these observations and whether they are real. Sites with Soil Orders Gley, Organic and Recent were limited to 10 sites and, although this represents their dominance within the Auckland Region 5, 2, 14% (NZLRI 2010), respectively, it is recommended that the number of sites representing these Soil Orders be increased to determine if a larger sample size would give similar outcomes. This would also ensure a more balanced design whereby each land use is balanced for Soil Order to determine if relationships exist between the factorial interaction of land use and Soil Order for trace element concentrations.

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 do not get 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 it is reinforced to sample indigenous sites to capture those naturally occurring background concentrations in soils. Councils should include trace element and Soil Order relationships to determine if similar outcomes are observed across various regional councils and build more knowledge on the role Soil Orders can play on trace elements. That said, it has also been suggested that soil bulk density should be considered when setting upper limits for trace elements when comparing concentrations of trace elements with Soil Order (Taylor *et al.* 2007). These authors reported that concentrations of cadmium can be overestimated for light, fluffy soils (eg, Organic soils, as was the case in the current study), but when based on volumetric measurements concentrations are similar to that found in heavier, dense soils.

There were no significant differences between trace element concentrations in the 39 sites that were sampled before 2000 and between 2008-11, except for mercury (Table 4). Concentrations of mercury increased from 0.11 mg/kg to 0.27 mg/kg for sampling periods before 2000 and between 2008-11, respectively, which could be associated with historic and/or present P fertiliser as described above. The increase is more likely to reflect the latter as the increase was picked up in the more recent 2008-11 sampling events. This is an example of the importance of re-sampling sites at least every five years (Kim and Taylor 2009) to not only detect changes over time but to build closer relationships with landowners to attain land management information that can help explain changes in concentrations of trace elements. Future research should also concentrate exploring trace element concentrations with soil depth to determine whether atmospheric transport and deposition are significant sources of these analytes. It would be expected that concentrations would be greater in topsoil if that is the case or that atmospheric inputs would be a contributing factor for greater concentrations in topsoil. However, Waikato Regional Council transect data at two soil depths showed on average mercury was significantly (P=0.032) lower in topsoils (average 0.13 mg/kg at the 0-10cm soil depth) compared with subsoils (average 0.16 mg/kg at the 10-20cm soil depth, Matthew Taylor, pers. comm.). Similarly, it would be important to assess and quantify the concentrations of trace elements in urban Auckland in various locations such as urban forests, industrial sites, schools, parks and high traffic areas to determine how heavily built up areas and anthropogenic impacts can affect trace element concentrations. Results should be compared to those for rural Auckland presented in this report.

Table 4. Changes in trace element concentrations for sites that were sampled before and after 2000 in the Auckland Region

First sampled year	Second sampled year	Land use	Site number	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1999	2009	Dairy	38	0.5	0.2	3.0	3.0	0.1	2.0	8.0	4.0
1999	2008	Horticulture	41	-0.2	0.3	-3.0	4.0	0.0	0.8	4.0	39.0
1999	2009	Dairy	42	-0.6	0.3	2.0	10.0	0.1	1.6	0.0	3.0
1999	2009	Dairy	43	0.8	-0.1	0.0	2.0	0.1	0.5	9.0	24.0
1999	2010	Drystock	46	1.7	0.2	1.0	6.0	0.3	0.5	-34.0	37.0
1999	2009	Dairy	47	-1.0	0.1	0.7	-0.6	0.2	0.2	-2.0	6.0
1999	2010	Drystock	48	-0.5	0.0	-2.8	-1.6	0.0	-0.5	-1.0	-7.0
1999	2010	Drystock	50	-0.2	0.0	0.0	-0.5	0.4	0.2	0.4	44.0
1999	2010	Drystock	51	-0.1	0.0	0.1	1.6	0.4	0.0	2.0	35.0
1999	2009	Dairy	53	0.2	0.0	2.2	1.0	0.0	1.8	0.2	-8.0
1999	2009	Dairy	55	0.8	-0.1	0.1	5.0	0.1	-0.3	-1.4	20.0
1999	2011	Forestry	58	4.3	0.8	-2.9	1.3	0.4	0.3	-0.6	30.0
1999	2011	Forestry	60	-0.6	0.8	0.1	1.7	0.4	1.0	0.9	40.0
1999	2010	Drystock	61	0.2	0.2	-4.0	1.5	0.4	-0.6	-0.6	5.0
1999	2009	Dairy	62	-4.0	-0.1	-4.6	-3.1	-0.1	-0.8	-7.6	-10.0
2000	2010	Drystock	63	-15.6	0.1	-9.0	-11.0	0.3	1.2	-18.0	-26.0
2000	2009	Dairy	64	-0.1	0.0	0.0	6.0	0.2	-0.6	2.0	0.0
2000	2008	Horticulture	65	1.0	0.1	1.0	3.0	0.0	1.6	1.0	9.0
2000	2009	Dairy	66	0.4	-0.1	3.0	16.0	0.1	0.7	2.0	7.0
2000	2008	Horticulture	67	1.8	0.2	4.0	3.0	0.0	0.9	9.0	34.0
2000	2008	Horticulture	68	1.2	0.0	-1.0	-2.0	0.0	-0.5	-2.0	-4.0
2000	2010	Drystock	69	1.3	0.0	2.0	0.0	0.2	0.2	4.0	5.0
2000	2008	Horticulture	70	1.9	0.1	2.0	4.0	0.1	1.7	8.0	15.0
2000	2008	Horticulture	71	-0.4	0.0	2.0	1.0	0.0	0.6	1.0	2.0
2000	2011	Forestry	72	0.8	0.8	1.5	3.0	0.4	3.2	1.0	47.0
2000	2009	Dairy	73	1.4	0.0	0.0	1.0	0.0	-2.7	0.4	-2.0
2000	2010	Drystock	74	-1.8	0.0	1.0	3.0	0.4	-0.2	0.2	2.0
2000	2009	Dairy	75	0.8	0.0	2.0	1.0	0.3	6.2	5.0	17.0
2000	2010	Drystock	76	0.6	0.2	-0.4	-1.2	0.7	0.6	2.1	-27.0
2000	2009	Dairy	77	-0.2	-0.1	-0.5	-3.0	0.1	14.9	5.4	1.0
2000	2010	Drystock	78	0.3	-0.2	-6.0	-4.7	0.4	-0.5	2.0	-8.0
2000	2008	Horticulture	79	-0.1	0.0	1.0	-1.0	0.0	0.8	-0.2	-4.0
2000	2008	Horticulture	80	0.1	0.0	3.0	4.9	0.0	0.1	0.1	6.0
2000	2008	Horticulture	81	0.2	0.0	0.0	-1.6	0.0	0.0	48.1	-2.0
2000	2008	Horticulture	82	0.3	0.0	4.4	-12.0	0.0	0.1	2.2	1.0
2000	2010	Drystock	84	0.5	0.1	-13.0	-2.3	0.4	0.7	-2.7	2.0
2000	2008	Horticulture	86	-0.1	0.0	0.4	0.0	0.0	0.7	0.4	-4.0
2000	2008	Horticulture	87	0.5	0.0	-0.1	10.0	0.0	0.3	3.7	7.0
2000	2008	Horticulture	88	1.0	0.0	0.8	-7.0	0.0	-0.1	0.2	2.0
	Mean			-0.1	0.1	-0.3	1.1	0.2	0.9	1.3	8.8
	Significance			ns	ns	ns	ns	$P<0.001$	ns	ns	ns

4.0 Conclusions, recommendations and future research

Although, all trace element mean concentrations did not exceed recommended guidelines for environmental soil health, nine soil samples exceeded the guideline range (with number of samples in parentheses) which included arsenic (1), cadmium (4) and copper (4) and this can have implications on the life-supporting capacity of soil. These findings were comparable to findings reported by other regional councils for rural soils in New Zealand.
Concentrations of trace elements were also significantly different for land use and Soil Orders.

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. Future research should also focus on characterising the parent mineralogy of the underlying rock to further ascribe background trace element concentrations.
- 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. Green areas in the urban environment provide aesthetic and recreational values, they mitigate flooding and regulate green house 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.
- Determining if or how atmospheric transfer and deposition influence concentrations in urban Auckland.
- Lastly, all 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 to 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.

5.0 Acknowledgements

The authors thank landowners for allowing access to their properties and providing information on their land management practices. Doug Hicks and Wim Rijkse are thanked for original soil descriptions and identification, as are the reviewers for their time.

6.0 References

ARC (2001). *Background concentrations of inorganic elements in soils from the Auckland region*. Technical Publication 153. Auckland, New Zealand: Auckland Regional Council

Cavanagh J E, O'Halloran K (2006). *Development of soil guideline values protective of ecological receptors in the Auckland region*. Prepared for Auckland Regional Council. Landcare Research Contract Report: LC0506/065. Lincoln, New Zealand: Landcare Research

Cook P J, Freney R J (1988). Sources of cadmium in agriculture. In *Cadmium accumulations in Australian agriculture*. (J Simpson, W J Curnow editors) 4-19. Canberra, Australia: Bureau of Rural Resources

Councell T B, Duckenfield K U, Landa E R, Callender E (2004). Tire-wear particles as a source of zinc to the environment. *Environmental Science and Technology,* 38, 4206-4214

Curran-Cournane F (2012). *Soil quality of plantation forestry sites in the Auckland region 2011*. Auckland Council Technical Report 2012/022 (pending). Auckland, New Zealand: Auckland Council

ECan (2006). *Background concentrations of selected trace elements in Canterbury soils*. Environment Canterbury New Zealand. Report prepared by Tonkin and Taylor Ltd. Job 50875.

Gaw S (2002). *Pesticide residues in horticultural soils in the Auckland region*. Auckland Regional Council Working Report 76. Auckland, New Zealand: Auckland Regional Council

Gaw S, Wilkins A, Kim N, Palmer G, Robinson P (2006). Trace element and DDT concentrations in horticultural soils from the Tasman, Waikato and Auckland regions of New Zealand. *The Science of The total Environment,* 355, 31-47

GenStat (2011). *Genstat for Windows*. 14 edition. VSN International Ltd, Oxford

Godt J, Scheidig F, Grosse-Siestrup C, Esche V, Brandenburg P, Reich A, Groneberg D (2006). The toxicity of cadmium and resulting hazards for human health. *Journal of Occupational Medicine and Toxicology,* 1:22

Gray C (2011). *Trace element concentrations in some Marlborough soils*. Marlborough District Council Technical Report 11-002. Blenheim, New Zealand: Marlborough District Council

Gregory S J, Anderson C, Camps M, McManus M (2011). Remediation of historic sheep dip sites using biochar and phytoremediation methods. In: *New Zealand 2011 Biochar Workshop; opportunities, risks and acceptance* 10-11 February 2011, Palmerston North, New Zealand: Massey University New Zealand Biochar Research Centre

Guinto D (2011). *Trace elements in Bay of Plenty soils*. Bay of Plenty Regional Council, Environmental Publication 2011/16

Hewitt A E (editor) (1998) *New Zealand Soil Classification* Lincoln, New Zealand: Manaaki Whenua Press

Hill R B, Sparling G P (2009). Soil quality monitoring. In: *Land Monitoring Forum. Land and soil monitoring: a guide for state owned enterprise and regional council reporting*, 27-88, Hamilton: Land Monitoring Forum

Johansson K, Bergback B, Tyler G (2001). Impacts of atmospheric long-range transport of lead, mercury and cadmium on the Swedish forest environment. *Water Air and Soil Pollution,* 1, 279-297

Kim N D, Taylor M D (2009). Trace element monitoring. Chapter 5 in: *Land Monitoring Forum. Land and Soil Monitoring: A guide for state owned enterprise and regional council reporting*

Longhurst R D (2006). *Soil cadmium*. Envirolink 73-HBRC 9. Report prepared by AgResearch for Hawkes Bay Regional Council

Longhurst R D, Roberts A H C, Waller J E (2004). Concentrations of arsenic, cadmium, copper, lead and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, 47, 23-32

MAF (2008). *Report one: cadmium in New Zealand agriculture report of the cadmium working group August 2008*. Wellington: Ministry of Agriculture and Forestry, Information Services

McLaren R G, Cameron K C (editors) (1996). *Soil science. Sustainable production and environmental protection* 2nd edition. Oxford: Oxford University Press

Molloy L (editor) (1993). *Soils in the New Zealand landscapes: the living mantle*. New Zealand Society of Soil Science. Canterbury, New Zealand: Lincoln University

NZLRI (2010). *New Zealand Land Resource Inventory NZLRI*. Landcare Research http://lris.scinfo.org.nz/#/layer/79-fsl-new-zealand-soil-classification

NZWWA (2003). *Guidelines for the safe application of biosolids to land in New Zealand.* Wellington, New Zealand: New Zealand Water and Wastes Association

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

Robinson B, Clothier B, Bolan N S, Mahimairaja S, Greven M, Moni C, et al (2004). SuperSoil: 3rd Australian New Zealand Soils Conference, 5-9 December 2004, Sydney: University of Sydney. Published on CDROM. Website www.regional.org.au/au/asssi

SigmaPlot (2011). *Version 12.0 for Windows*. Chicago

Sorensen P (2009). *Annual soil quality monitoring report for the Wellington region, 2008/09*. Greater Wellington Regional Council publication, GW/EMI-G-09/237

Sorensen P (2010). *Annual soil quality monitoring report for the Wellington region, 2009/10*. Greater Wellington Regional Council, publication GW/EMI-G-10/165

Steinnes E (2010). Human health problems related to trace element deficiencies in soil. In 19th World Congress of Soil Science. 1-6 August 2010, Brisbane, Australia, R J Gilkes, N Prakongkep, editors

Taranaki Regional Council (2005). *Cadmium in Taranaki soils. An assessment of cadmium accumulation in Taranaki soils from the application of superphosphate fertiliser.* Stratford, New Zealand: Taranaki Regional Council

Taylor M (2012). *Soil quality and trace element monitoring in the Waikato region 2010.* Waikato Regional Council document number 2090445

Taylor M, Gibb R, Willoughby J, Hewitt A, Arnold G (2007). *Soil maps of cadmium in New Zealand*. Hamilton, New Zealand: Landcare Research

Taylor MD (2011) *Towards developing targets for soil quality indicators in New Zealand: Findings of a review of soil quality indicators workshop, 6th May 2011*. Unpublished report, Land Monitoring Forum

Taylor M D, Kim N D, Hill R B, Chapman R (2010). A review of soil quality indicators and five key issues after 12 year soil quality monitoring in the Waikato Region. *Soil Use and Management* 26, 212-224

Zheng Y M, Liu Y R, Hub H Q, He J Z (2008). Mercury in soils of three agricultural experimental stations with long-term fertilization in China. *Chemosphere* 72, 1274-1278