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Trends in selected trace element monitoring data in the Waikato Region 2001-2022.

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Abstract

This report presents trends in data from soil quality monitoring sites and identifies and discusses the main trace element issues facing the rural parts of the Waikato Region. Urban land has not been assessed in this report due to the small proportion of land in urban land use (<5%) and issues around access and privacy.

A suite of 33 elements, extracted by acid digestion and total fluoride were measured at 154 soil quality sites in the Waikato region. Measured results were compared against New Zealand guideline values for human health and the protection of ecological receptors, where these exist. Otherwise, reputable guideline values from overseas guidelines were identified using MfE criteria.

The main trace elements issues identified were:

1. Some trace elements (As, Cd, Cu, Tl, Zn) were found to be near or above guideline values for the protection of human health and the environment at some sites.
    a. Of these, Cd is currently of greatest concern within the Waikato region due to the extent of Cd accumulation in soil, the risk of exceeding food standards for some crops and animal products, potential restriction on land use and farm production, and contamination of the wider environment including soil, surface and ground waters, estuaries and lakes. There is only one major source of Cd to rural land, phosphate fertiliser, which contains Cd as a contaminant. Waikato regional council should continue to support and maintain membership of the Cadmium Management Group to provide leadership for managing Cd.
    b. The elements As, Cu and Zn form a group of priority contaminants well known to environmental managers. A common feature of this group is that they have multiple sources, which complicates developing comprehensive management for any one of these elements. Instead, a source-by-source approach may be more effective, e.g. timber that does not require treatment with CCA, breeding animals resistant to facial eczema.
    c. An emerging trace element issue may be Tl as it exceeded the guideline value at several sites and under different land uses. Confirmation that Tl is or is not an emerging issue is required.

2. Other trace elements (Co, Cu, Mo, Zn) are at or close to levels where deficiency could occur at some sites. These are usually well known for productive land uses with management techniques available to overcome deficiencies. Cu and Zn are remarkable as they can be an issue from excess due to contamination, as well as deficiency due to naturally low Cu or Zn contents for specific soil types.

3. There are some trace elements (F, Tl, U) for which there is limited information on their environmental effects, e.g. despite the high ranking of F in priority listings and the occurrence of animal health issues, there is no accepted guideline value for total F in soil, although Cronin (2000) and Cavanagh (2019) have provided indicative guidelines based on limited data. Similarly, chemical toxicity guideline values for U are lacking as current guideline values are based on radioactivity and do not include U’s chemical toxicity, and these were also designed for other countries.

Advice should be provided to landholders when the soil guideline values are exceeded, or trace element concentrations are at or close to levels where deficiency could occur. Further research into the ecotoxicity trace elements with little or no New Zealand risk-based data should be encouraged to inform risk-based soil guideline values. Further study to establish if Tl is an emerging issue should be undertaken. Developing alternatives to known trace element contaminants should be encouraged (e.g. timber that does not require treatment with CCA, breeding animals resistant to facial eczema and kiwifruit vines resistant to PSA).

1 Introduction

1.1.1

Waikato Regional Council (WRC) recognises that the region's economy and people's wellbeing depend on our natural capital, including soils, and has legislative responsibility to manage the soil resource. An established soil quality monitoring programme provides information for State of the Environment (SOE) reporting, policy development, and helps in understanding the interactions between soil and water. Samples taken as part of this programme were also analyse for a suite of trace and major elements. Trend measurements of trace elements have been analysed to assess the sustainability of current land use activities and the effectiveness of WRC policies by providing evidence of change or stability.

Trace elements are naturally present in the environment and in soils they are inherited from the parent material. However, concentrations of trace elements in soils are constantly being altered due to natural phenomenon, e.g. volcanic activity (Godt et al. 2006), or human-derived inputs, e.g. soil amendments (Longhurst *et al.* 2004; Taylor et al. 2010). A healthy soil will possess optimal trace nutrient levels, with low concentrations of harmful trace elements, among other characteristics, such as optimal pH, and soil organic matter, good aeration and water infiltration and storage. Soils with optimal levels of trace elements have well-functioning soil microbial communities benefitting the biogeochemical cycling of nutrients and the growth of plants. Harmful levels of trace elements resulting in contamination can also be a health risk for animals and humans (National Academies of Sciences, Engineering, and Medicine 2024).

Many soils in the Waikato region are naturally low in some trace elements (Co, B), or have high levels of potentially toxic trace elements (As from geothermal activity), while power plants, industry and traffic contribute to the trace element load (Khan et al. 2021). Thermal power plants were a feature in the Waikato region and geothermal plants remain currently active. Many agricultural chemicals used in the region contain trace elements, while phosphate fertiliser is a major source of Cd, F and U. Cities present in the region and the roading network, (SH1, SH2, SH3) contribute traffic-related trace elements.

Preliminary development of the soil quality programme was carried out in collaboration with Manaaki Whenua – Landcare Research from 1995 with regional coverage achieved by 2005. This programme is aligned with national soil quality monitoring as established and administered through the Land Monitoring Forum (LMF). Several regional councils across New Zealand have begun to monitor and report the concentrations of trace elements across various soils and land uses, e.g. Auckland Regional Council (ARC 2001); Marlborough District Council (Gray 2011); Greater Wellington Regional Council (Drewry et al. 2021).

This report presents trends in the data since 2007 and discusses the main trace element issues facing the Waikato Region. The current report investigates the concentrations of trace element in soil under common land uses and soil orders in rural Waikato. Analysis using mixed modelling techniques is presented for 2001-2016. Urban land has not been assessed in this report due to the small proportion of land in urban land use (<5%) and issues around access and privacy.

2 Methods

2.1 General Methods

The WRC soil quality monitoring programme is a screening tool or early warning system designed to gather a large amount of information quickly and at a low cost to inform detailed environmental assessment of the region's soils. It is also useful to inform the aspirations of Māori to sustain the mauri of the soil. According to Cavanagh & Hamsworth (2022), 'Mauri' refers to an internal essence, vitality, or life force; for example, a healthy, functioning soil 'fit for purpose' and sustaining life, energy, well-being, and health (mauri ora, whenua ora). It is often used to refer to the capacity or condition of a soil to function as a living, healthy ecosystem that can sustain mauri. Currently there are 154 long-term monitoring sites (Figure 1) and it takes 5 years to sample the whole set (about 30 sites sampled per year). Each annual sampling contains a mix of land uses to minimise the effect these would have if, say, all forestry sites were sampled in one year. Details of the programme design and sampling can be found in Taylor & Cox (2021).

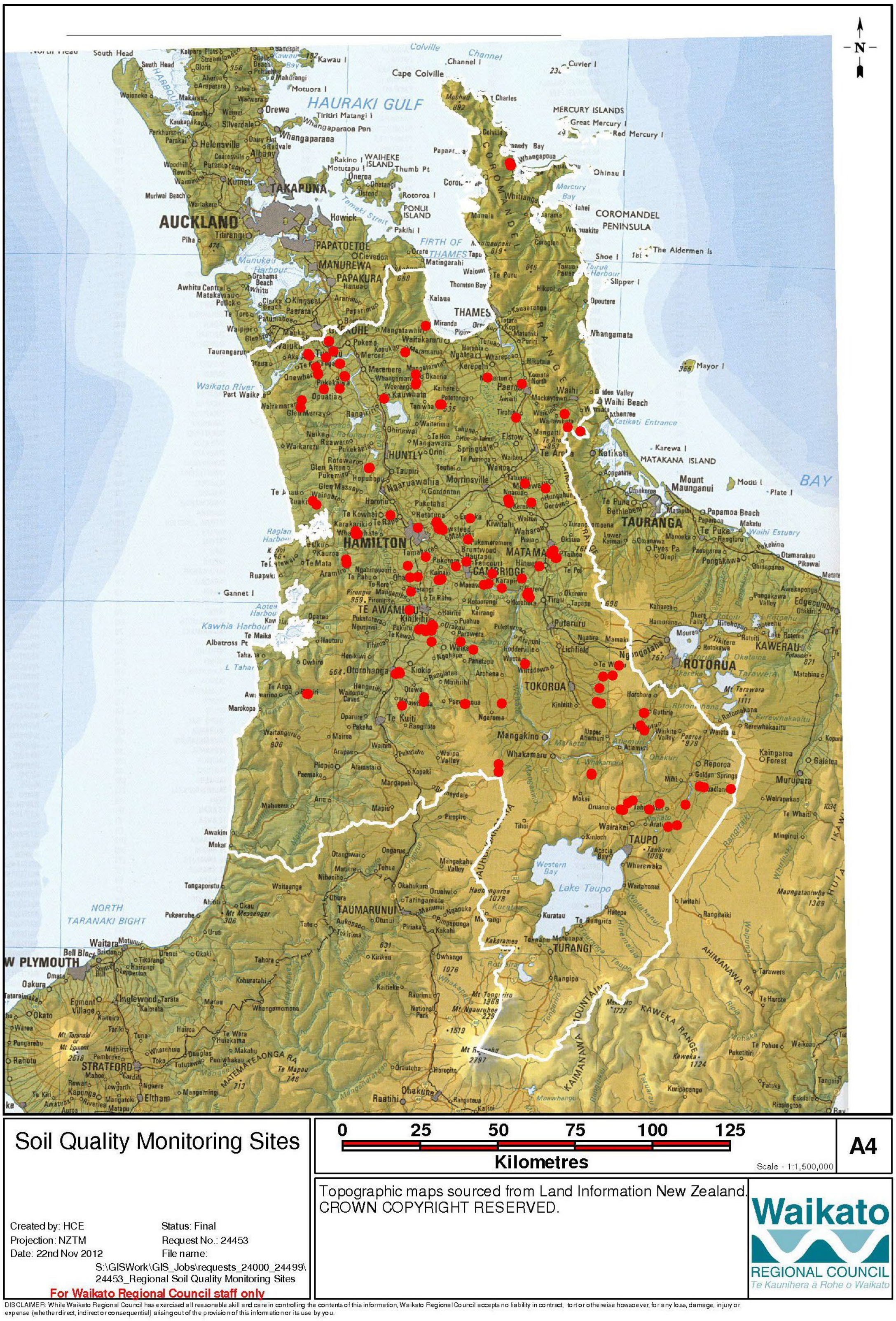

Figure 1: **Map of soil quality site locations.**

All analyses for trace elements were carried out at Hill Laboratories, Hamilton following the Metals extensive suite for 33 elements, extracted by nitric/hydrochloric acid digestion (method US EPA 200.2) and measured by inductively coupled plasma- mass spectrometry at trace level. In addition, total fluoride was extracted using alkaline fusion and measured using an ion selective electrode (Methods of Soil Analysis 2nd Edition, 1-27 Pt2, 26-4.3.3).

Considerable improvement in detection limits occurred about 2003 due to the purchase of improved instrumentation. This impacted elements with concentrations near the detection limit. These elements were Sb, Mo and Ag. Repeat sampling, to complete a round of all sites, so to take advantage of these improved detection limits, took until 2007, thus data for Sb, Mo and Ag are presented from 2007 on.

Results were compared against the New Zealand Soil Contaminant Standards using the rural residential scenario (25% of produce consumed is home-grown) and the protection of ecological receptors for non-food production and agricultural land (Eco-SGVs, Cavanagh 2019), where these exist. Otherwise, the MfE environmental guideline values database https://environment.govt.nz/facts-and-science/land/environmental-guideline-value-egv-database/ was used to identify the most reputable guideline from overseas guideline values. The Eco-SGVs are protective of 95% of the crop and grass species and 80% of soil invertebrates. Tillage and the use of pesticides/herbicides make it unrealistic to protect 95% of soil processes and soil invertebrates and therefore only 80% of these are protected.

Cavanagh & Hamsworth (2022) evaluated the implementation of the ecological soil guidelines values of Cavanagh (2019) for soil quality assessment. They proposed simplifying the application of Eco-SGVs for regional council state of the environment monitoring to a target limit of 95% protective of ecological receptors and are considered the concentration below which no more than minor effects will occur.

2.2 Sites

Soils were sampled at each monitoring site following the methods in the LMF national guidelines (Hill & Sparling, 2009). The same sampling methodology was followed to ensure consistency between results gathered from different regions and over time. Initiation of soil quality monitoring was in 1995 with 3 sites. The number of sites was increased to cover the area of the geographic area of the region, major soil types and main land uses. The number of sites reached 150 in 2011 and this number of sites is approximately maintained.

Sites were lost for monitoring due to urban expansion, and being built over, or due to landholders withdrawing from the monitoring programme. The number and types of sites are reviewed during each reporting period and additional sites added to keep the total number of sites around the 150 target and to cover all the geographic region, major soil types and main land uses. Sites monitored for only a short time were removed from the dataset.

Soils were classified according to the New Zealand Soil Classification (Hewitt et al. 2010). Soil orders and number of sites were Allophanic (54 sites), Brown (18), Gley (20), Granular (16), Organic (5), Podzol (5), Pumice (26), Recent (6), Ultic (4).

Land use classes were based on the current land system, i.e. pastoral farms were predominantly in pasture but a crop, such as maize, could be grown during pasture renewal as this a common practice. Several sites changed land system over the twenty-year period of monitoring. Nine sites changed from production pine forestry to pasture, one site changed from drystock to production forestry, five sites changed from intensive vegetable cropping for several years to pasture, five sites changed from maize cropping for several years to pasture, and one site had just changed from an apple orchard to maize growing. These groupings were too small to be statistically analysed. Note, it is a common practice to “restore” land exhausted by cropping by putting it into pasture. Where these changes occurred, the land was classified as the original land use system for the first sampling after change and subsequent samplings were classified as the new land use system.

Land systems used were pasture (83 sites), arable (annual cultivation, 15), perennial (perennial plants left in place, 12), production forestry (25) and native (indigenous vegetation, 15). The land managements and land uses covered under each land system are presented in Table 1. Initially, the pasture classification was separated into dairy (milking cows) and pasture used for meat or fibre production. However, it has become more difficult in recent times to separate these two classifications as farms have diversified and the indicator results for both these land uses have come together, e.g. dry dairy cows are often run on what was previously only sheep and beef farms.

Table 1. Land managements and land uses covered under each land system

Land System	Land managements
Native	Native forest
Forestry	Production pine forest
Arable	Vegetable production, grain production and rotations including both.
Perennial	Apple and kiwifruit orchards
Pasture	Pasture species for animal (cattle, sheep, deer, goats) grazing, including cut and carry for barn fed animals (goats). Can include a fodder crop such as plantain or beet.

2.3 Statistical Analysis

Each trace element was assessed using Genstat 21.1 (The Numerical Algorithms Group and Rothamsted Research) for statistical trends using linear mixed modelling with random splines overall (shortened to “mixed modelling” in the results and discussion sections), by soil order and by land use. Mixed modelling has greater ability to identify trends than using raw, measured data alone and corrects for bias from the different numbers of samples in each category, e.g. there are many pasture sites but fewer perennial sites. Data for mixed modelling required log transforming to get approximate constancy and normality of the residual variation. The back-transformed estimates were “bias-corrected” to make this the same as the overall arithmetic mean of all the original values in the data.

Random terms were used to give an appropriate structure to the error terms, allowing for the correlations arising from repeated observation of the same sites. Random smoothing spline terms were used in the model for three reasons: firstly, they allowed fitting trend terms that are data driven, not requiring the choice of a particular functional form, secondly, they allowed estimation of the trends as if every site had been measured at every date, and finally they allowed modelling the serial correlation between successive observations on the same sites. The accuracy of estimated values in any one year was improved by utilising the information from sites before and after each time period, thus increasing the effective sample size (Appendix I). Patterns and trends between 2001 and 2016 or 2007-2016 for Sb, Mo and Ag, calculated by this method are presented in the results section. Note that the patterns and trends are to provide guidance, not to calculate concentrations. The quantity of a trace elements is provided by the measured values.

The 5-yearly rolling average of the measured values were also calculated. It takes 5 years to sample all 154 sites in the soil quality monitoring programme. The 5-yearly rolling average used the most up to date data for each site.

3 Trace Element Results and Discussion

3.1 Preamble

Although total F and 33 other elements were measured, not all elements are relevant to regional council monitoring. Elements are reported in order of relevance. The National Environmental Standard for Soil Quality and Trace Elements (NEMS 2022) identifies eight trace elements to be assessed: As, Cd, Cr, Cu, F, Ni, Pb and Zn. Results for these elements are presented first followed by result for other trace elements of note within the Waikato region, e.g. B, Co and Mo are presented because they are key micronutrients that are often deficient in agricultural soils. Tl is presented due to enhanced levels identified and the possibility that it is an emerging contaminant. U is presented as it is from the same source ad Cd and F and so is presented for completeness. Other elements measured as part of the analytical suite, but with results of lesser interest for this monitoring report are detailed in Appendix 1. Additional and more in-depth assessment of each element and potential interactions across other domains are also detailed in Appendix 1.

Results presented are partitioned into concentrations at the most recent time and trends over the long term. Each element is assessed against guideline values for human and ecological health, examining the overall dataset, then soil order and land use, to identify the trends for each element and to identify where possible drivers to change are occurring.

The following principles were used in choosing Guideline values. It is preferable to use NZ risk-based guideline values rather than overseas guideline values to take New Zealand's unique flora and fauna into account. Where risk-based guideline values are not available then other New Zealand guideline values should be used and if these are not available than other international guideline values should be used (MfE 2011).

For human health, the Soil Contaminant Standards using the rural residential scenario (25% of produce consumed is home-grown) (MfE, 2011a) was used for As, Cd, Cr, Cu, Pb, as agricultural soil is not included in the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health and the rural residential scenario is the nearest approximation. International risk-based guideline values for agricultural soil were assessed to provide comparison and confirm the use of the lifestyle block guideline values was reasonable for each element. As there is no New Zealand Soil Contaminant Standards for Zn or Ni, the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health nickel and zinc in agricultural soil (CCME 1999) and the USA Ecological Soil Screening Level protective of ecological receptors for nickel (USEPA, 2007) (38 mg/kg) were identified from the Ministry for the Environment spreadsheet of guidelines. The CCME guideline value for Cu was 63 mg/kg, for Ni it was 50 mg/kg and for Zn it was 200 mg/kg. The CCME is a combined human health and environmental protection guideline, and it is likely the environmental considerations are dominating. In comparison, the USEPA screening level value for Ni was 38 mg/kg. For ecological values, the NZ soil guideline value for agricultural soils for the protection of ecological receptors was used (Cavanagh 2019) for As, B, Cd, Cr, Cu, Pb and Zn. Cavanagh (2019) was unable to develop a reliable guideline for F due to insufficient data.

3.2 Current State: Results at the time of most recent sampling

3.2.1 Land use impacts

Highlights

There were clear land use effects seen in the most recent sampling of sites, although effects varied depending on the element. The lowest median concentrations of trace elements were found in native and forestry land uses except for Cr and Sb, which both showed no elevation in concentration across land uses. Land under perennial had the highest median As, Cd, Cu, Zn, B, Co, F, Ni, Ag and Tl concentrations. Of note was a very high Cu value at an established apple orchard. Land under arable land use had the highest Pb, Mo, Hg, Sn and U. Also of note was extremely high Pb and Sb values at one arable site. This result was attributed to one site having been a rifle range prior to becoming a farm. Another site with more moderate Pb and Sb values was also identified as a previous rifle range. One pastoral site had very high Zn, about 5 time the median, although no clear source could be identified.

Results are presented in three groupings, elements included in the National Environmental Monitoring Standard for Soil Quality and Trace Elements, micronutrient elements, and the lesser-known elements.

Elements included in National Environmental Monitoring Standard for Soil Quality and Trace Elements

Arsenic

There were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$) for As. Granular soils, which contain high concentrations of iron minerals, had consistently higher average As concentrations than other soils. Arsenic adsorbs mainly to amorphous iron oxyhydroxides so As is readily sorbed in Granular soils regardless of its source.

Soils under perennial land use also had consistently higher average As concentrations than other land uses although these soils were rarely Granular soils. There are many potential As sources associated with horticultural land including CCA-treated posts and the past use of As-containing pesticides like lead arsenate and monosodium methanearsonate (MSMA). Fortunately, As-containing pesticides are no longer used in New Zealand, but the higher levels of As in horticultural land maybe evidence of leaching from CCA treated framing or legacy As from past use of As-containing pesticides.

Two individual sites exceeded the Soil Contaminant Standards using the rural residential scenario (17 mg/kg) and the guidelines for the protection of ecological receptors (20 mg/kg). One was a very long-term apple orchard research station, likely to have received considerable amounts of As-containing pesticides, and the other was a low-lying dairy pasture that was periodically flooded by the Waikato River, which contains As from natural geothermal discharges and discharges from geothermal power stations.

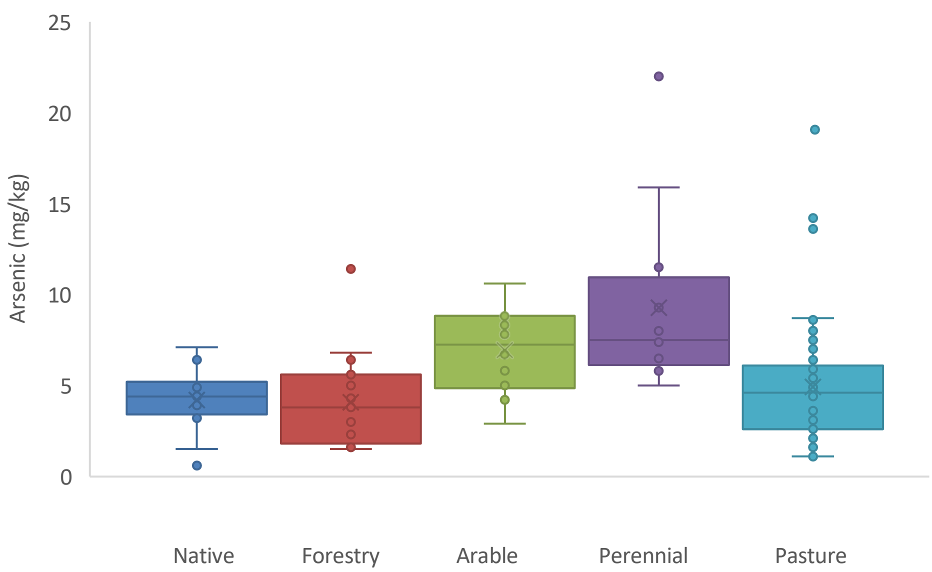

Figure 2. Boxpots of acid recoverable As (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region.

Cadmium

There were significant differences between land uses (p<0.01) and soil orders (P<0.01) for Cd. Allophanic and Granular soils had higher average Cd concentrations than other soil orders, while Podzol Pumice and Ultic soils had lower average concentrations. Both mixed modelling and measured 5-yearly rolling average showed perennial, arable and pasture have Cd concentrations well above native.

Intensive perennial and dairy farming are prominent land uses on Allophanic and Granular soils and apply large quantities of Cd-containing phosphate fertiliser. Land management is likely overriding any soil order effects. Taylor (2016), while investigating the fate of trace elements impurities in fertilisers, found the highest median Cd concentration in soil was in kiwifruit orchards, which are a high intensity crop so receive high P fertiliser inputs, e.g. applications of 1 t/ha superphosphate or reactive rock phosphate (RRP) + mixtures of "organic inputs". The large applications of RRP to organically farmed kiwifruit and corresponding elevation in soil Cd concentrations may be of particular concern to organic kiwifruit growers.

About a quarter of sites measured, including arable, horticultural and pastoral sites, had Cd concentrations exceeding Soil Contaminant Standards using the rural residential scenario of 0.8 mg/kg and 1 % of sites (intensive long-term dairy and kiwifruit orchards) exceeded both the Soil Contaminant Standards using the rural residential scenario and ecological receptors (1.5 mg/kg). These results reflect the long-term nature of Cd contamination, the history of large applications of Cd-containing fertilisers in the region; concerns already raised by Waikato Regional Council at the national level (Kim 2005).

However, the risk posed by Cd for various food crops is controlled by a complex web of soil factors, not just soil concentration. Cavanagh et al. (2019) highlighted the variation that can exist between sites and the challenge in applying generic Cd soil guideline values without considering other soil properties. Consistent with this finding, Gray et al. (2019, 2019a) reported no strong significant relationships were found between soil properties and Cd concentrations in grain or potatoes, respectively. However, there were significant differences between cultivars. A common finding in these New Zealand studies of Cd is that despite higher soil Cd concentrations found in the Waikato region, Cd in the food product was much lower than in some other regions. However, it is not clear if the lower than expected food Cd concentrations were due to cultivar effects or regional effects. Nevertheless, ongoing monitoring of Cd is important due to the risks to human health and land use flexibility.

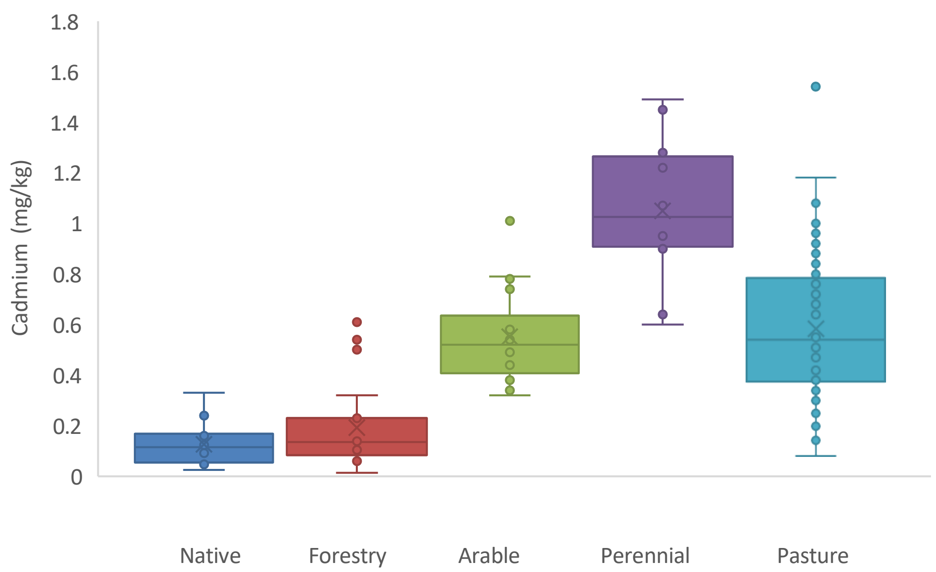

Figure 3. **Boxpots of acid recoverable Cd (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region**

Chromium

There were significant differences between land uses (p<0.01) and soil orders (P<0.01) for Cr. Mixed modelling soil order differences show Granular soils had considerably higher average Cr concentrations compared with the next highest soil orders (Brown and Gley soils). Granular soils have high concentrations of iron minerals that can form Cr minerals, so the high Cr is expected to be natural (Ma and Hooda 2010).

Mixed modelling showed perennial had higher average concentrations of Cr than other land uses. However, the higher concentrations of Cr in arable soils were nearly all on Granular soils, thus most of the Cr at these sites is likely natural and anthropogenic Cr (the atmospheric deposition flux, fertilisers, treated timber) is a much smaller contribution. All sites had Cr concentrations below the New Zealand Soil Contaminant Standards using the rural residential scenario and the protection of ecological receptors for Cr (VI), 290 mg/kg and 300 mg/kg, respectively.

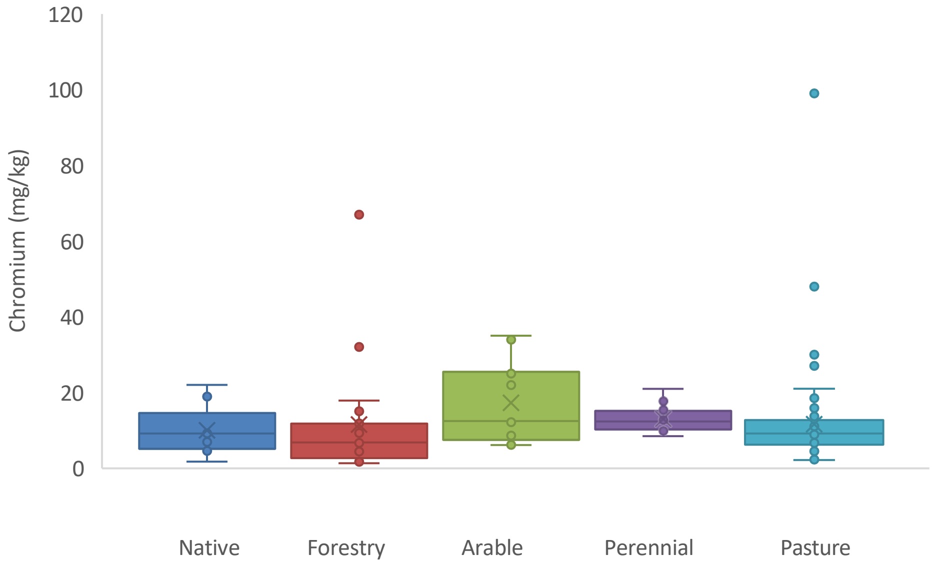

Figure 4.

Figure 4. **Boxpots of acid recoverable Cr (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region**

Copper

There were significant differences in the trend pattern for land use and between land uses (p<0.01) and between soil orders (P<0.01). Allophanic and Granular soil orders had had higher average Cu concentrations compared to other soil orders. Perennial is a prominent land use on Allophanic and Granular soils and land management with the application of large quantities of Cu-based agrichemicals, is likely overriding any natural soil effects. However, only one apple orchard currently exceeds the soil guideline value for the protection of ecological receptors (130 mg/kg).

High concentrations of Cu were measured in Lake Ngaroto, a peat lake, consistent with movement of Cu in DOM from peatland to the lake (Taylor 2016). The DOM fraction of SOM is mobile and has a great affinity for Cu (McGrath et al. 1988).

Sixteen Native, forestry and a pastoral site (about 3 %) had Cu concentrations below the level at which Cu deficiency could occur. However, only the pastoral site would likely be affected, and farming practices would mean these animals are likely receiving Cu supplements. Podzols, Pumice Soils, and Recent Soils derived from greywacke can be naturally low in Cu.

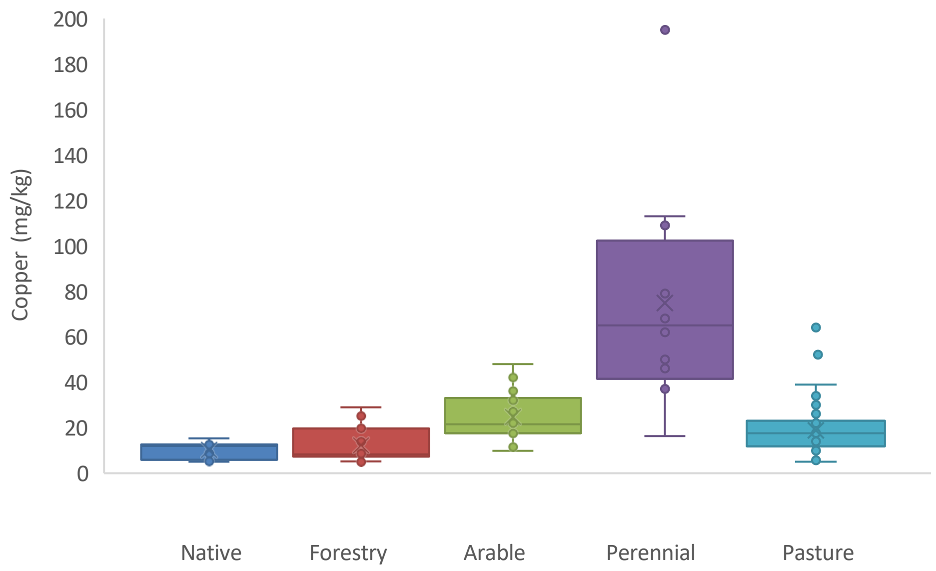

Figure 5. Boxpots of acid recoverable Cu (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Fluorine

There were significant differences between land uses (p<0.01) and soil orders (P<0.01) for F. The volcanic soil orders, Allophanic, Granular and Pumice soils, had higher average total F concentrations, while Podzol, Organic and Ultic soils had lower average total F concentrations. As a natural source of F in New Zealand is volcanic eruptions (Cronin et al. 2000), some F in Allophanic, Granular and Pumice soils may be volcanic in origin.

Fertilised land uses, arable, perennial and pasture, had higher total F concentrations than land in native land use, consistent with accumulation of F impurities of phosphate fertiliser. Recently, Wehrle-Martinez et al. (2024) reported sub-clinical fluoride toxicosis may be linked to spontaneous humeral fractures in first-lactation dairy cows in New Zealand.

F concentrations found in this study ranged from 70-900 mg/kg, which falls within the guidelines from two New Zealand sources. Cronin et al. (2000) estimated that for sheep, the tolerance limit for dietary F should be reached at soil F concentrations ranging from 370 to 1460 mg/kg, while for cattle the range was 330 to 1090 mg/kg. Cavanagh (2019) developed provisional added contaminant limits for F (130 mg/kg for agricultural land), but, given the uncertainty of the estimates, they are not recommended for use.

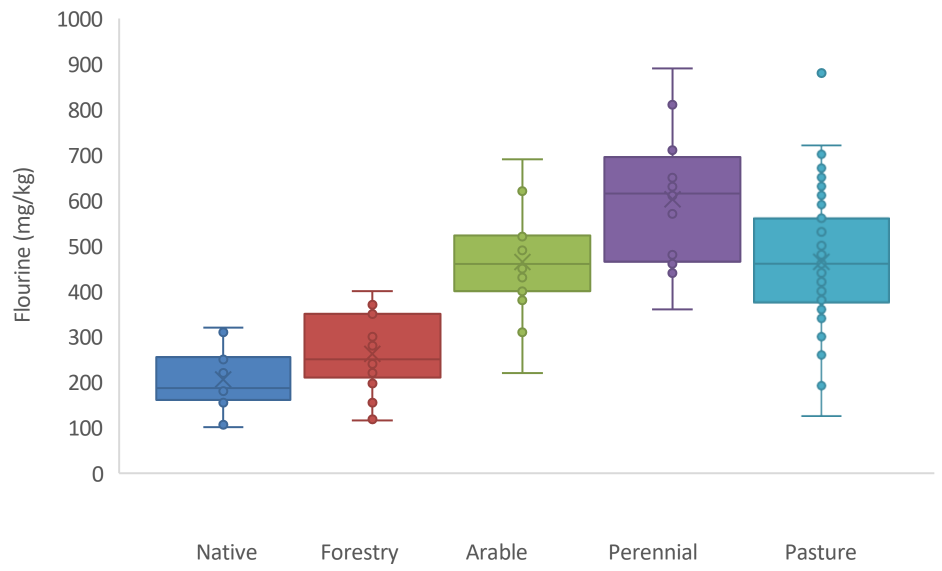

Figure 6. Boxpots of Total F (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Lead

There were significant differences between land uses (p<0.01) and soil orders (P<0.01). Average Pb by Soil Order showed Granular soils had higher average Pb concentrations, while Podzols, Pumice and Organic soils had the lower average Pb concentrations. Perennial and arable land uses had higher Pb concentrations, but results varied considerably suggesting Pb was particulate and not evenly spread through the soil.

An interesting issue that arose during monitoring were outliers in soils from past, often unrecorded, rifle ranges. Both Pb (lead in bullets) and Sb (in cartridge primer) concentrations were 100-fold higher than usual at these sites and are outliers, exceeding the soil guideline value for Pb for agricultural soils for the protection of ecological receptors (540 mg/kg). This data was compared with that in the WRC Hazardous Activities and Industries List, aerial photos and maps, and proved useful for identifying and locating two "lost" rifle ranges. Single sites under cropping, forestry, perennial and native land use have been identified and these outliers were excluded from analysis. Except for the suspected historic rifle range sites, all sites met the guideline value for agricultural soils for the protection of ecological receptors.

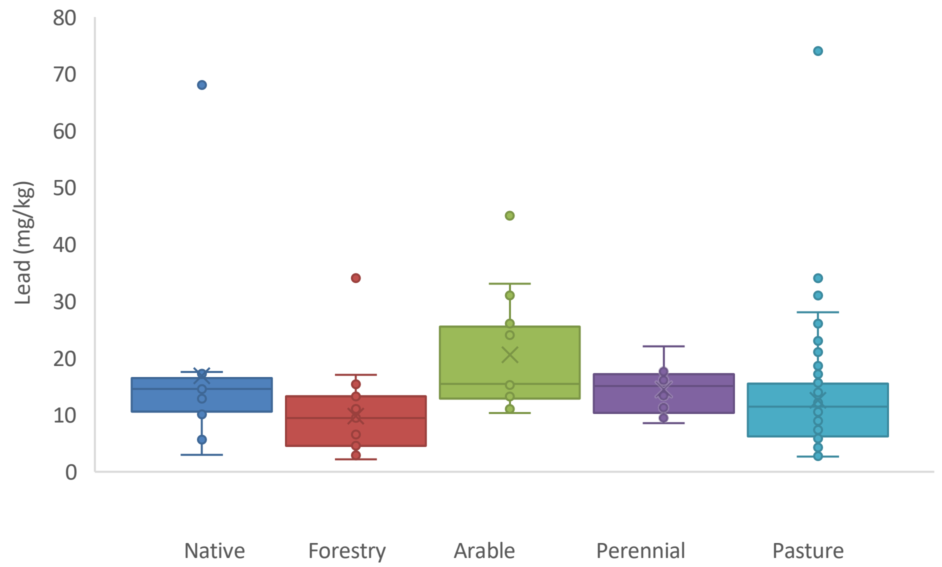

Figure 7. Boxpots of acid recoverable Pb (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region. One arable site with Pb of 750 mg/kg not shown

Nickel

There were significant differences between land uses (p<0.01) and soil orders (P<0.01) for Ni. Granular, Recent and Gley soils had higher average Ni concentrations than other soil orders, while Podzols, Pumice and Ultic soils had the lowest average concentrations. Land uses where fertiliser was applied (arable, perennial and pasture) had elevated Ni concentrations compared to non-fertilised land uses (native and forestry). Taylor (2016) reported Ni in phosphate rock used in New Zealand fertilisers ranged from 1-105 mg/kg, so fertiliser is the likely source. In comparison, Granular soils have high concentrations of iron minerals capable of adsorbing Ni and it seems likely that a large proportion of the Ni in Granular soils is natural (Taylor 2016; Ma and Hooda 2010; Salminen et al. 2005).

No New Zealand risk-based guideline was found for Ni but no sites exceeded the USA Ecological Soil Screening Level protective of ecological receptors (38 mg/kg) or the Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health in agricultural soils (50 mg/kg). Currently, there are no apparent issues with Ni in the Waikato region.

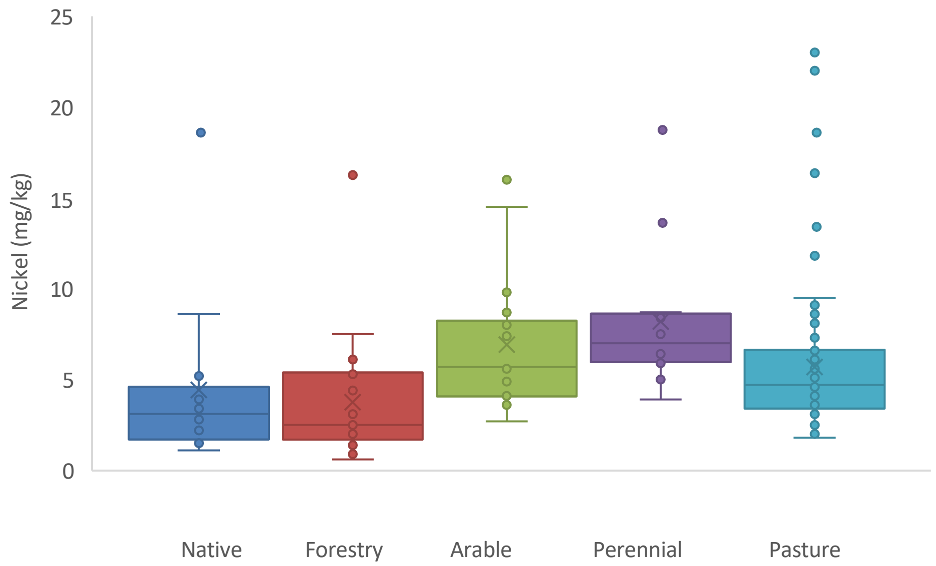

Figure 8. Boxpots of acid recoverable Ni (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Zinc

There were significant differences between land uses (p<0.01) and soil orders (P<0.01). Allophanic, Granular, Gley, Brown and Recent Soils had higher Zn concentrations, while Pumice, Organic, Podzols and Ultic soils had lower Zn concentrations. These results were expected as there are quite complex interactions between Zn and soil, and soil is acting as a sink and a source for Zn. Please refer to Appendix 1 for more detail on these chemical interactions.

Perennial had higher average Zn concentrations than other land uses and were consistently near the NZ soil guideline value for the protection of ecological receptors (Cavanagh 2019). Arable sites also had elevated average Zn compared with native sites, probably both land uses have similar agrichemical sources. Pasture sites had similar concentrations to arable, but these are likely from different sources, the treatment for facial eczema and other animal remedies (Kim & Taylor 2017). One pastoral site had very high Zn, about 5 time the median, although no clear source could be identified. Please refer to Appendix 1 for more detail on Zn sources. Monitoring of Zn should continue due to the number of sources of Zn and the current levels in soils.

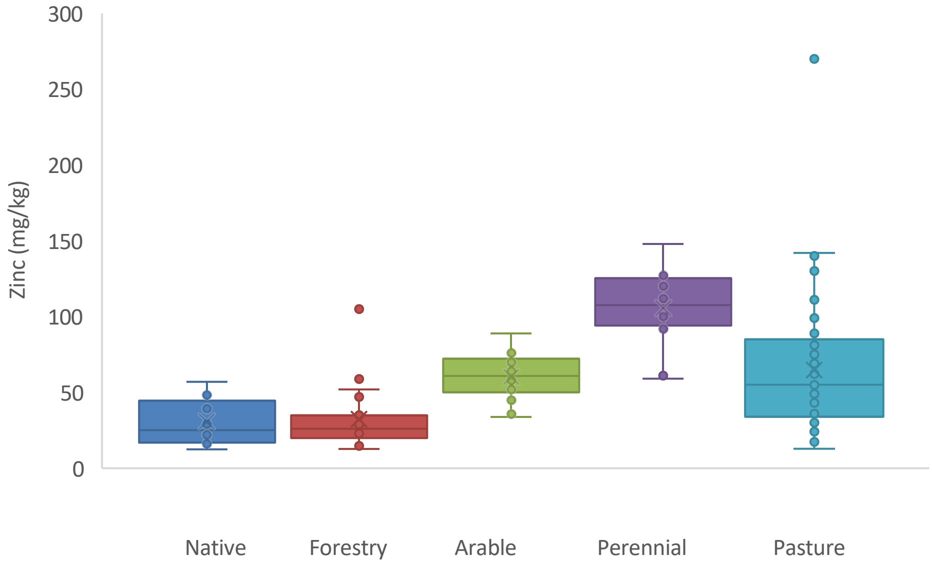

Figure 9. Boxpots of acid recoverable Zn (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Micronutrient elements

Boron, Cobalt and Molybdenum

B, Co and Mo are key micronutrients that can commonly be deficient in soils. Horticultural soils had higher average B concentrations than other land uses with significant accumulation in kiwifruit orchards. This is surprising as kiwifruit is a B sensitive crop and excessive B reduces fruit yield and premature ripening in cool storage (Smith et al. 1985). Boron can easily be transferred to surface water and some lakes and streams measured in Taylor (2016) periodically exceed the B trigger value for freshwater protection for 95% of aquatic species (0.37 g/m, ANZECC 2000). Interestingly, rainbow trout, an important game fish in the Waikato region, was the most sensitive fish species reported by WHO (1998) with NOECs ranging from 0.009-0.103 g/m.

Taylor (2016) also reported accumulation of B in estuarine sediments, consistent with the established view that B is incorporated into fine-grained sediments once it reaches the marine environment (Boon & MacIntyre 1968; Liss & Pointon 1973). So, accumulation of B in sediments may impact marine aquatic life.

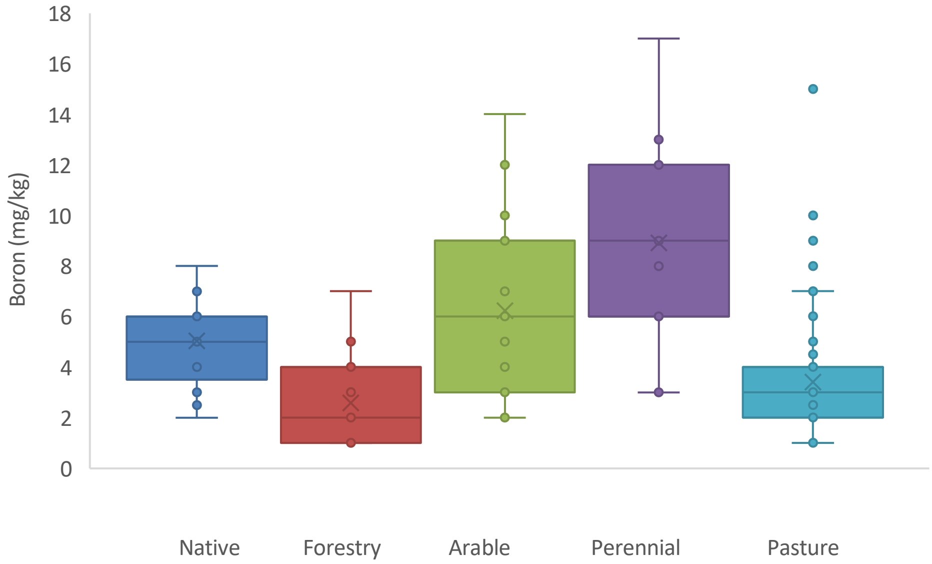

Figure 10. Boxpots of acid recoverable B (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

About a quarter of sites have Co concentrations below the deficiency level of < 2 mg/kg for animals (Hawke et al. 1994). No other issues with Co were identified.

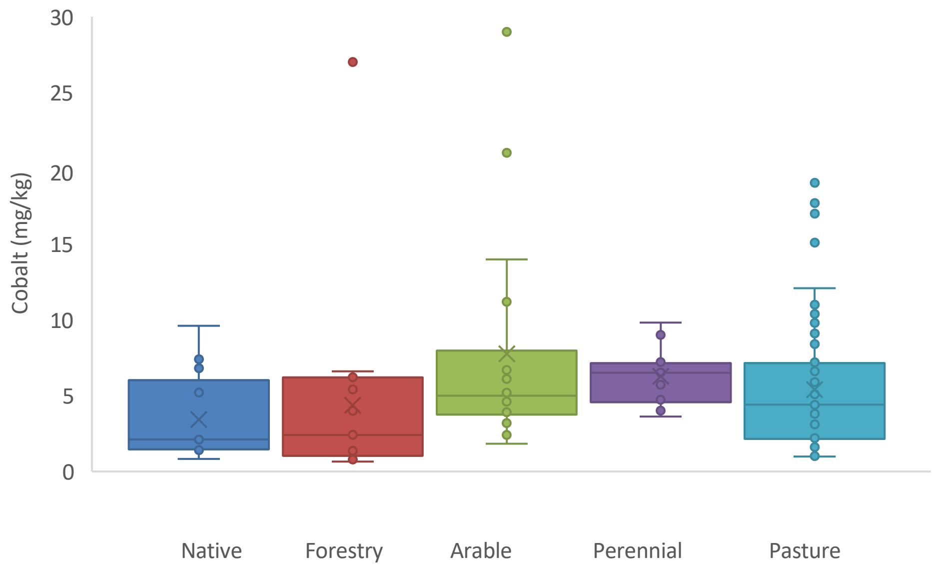

Figure 11. Boxpots of acid recoverable Co (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

No significant differences between land uses or soil orders were observed for Mo. However, Mo was slightly higher in soil under arable and in Granular and Allophanic soils.

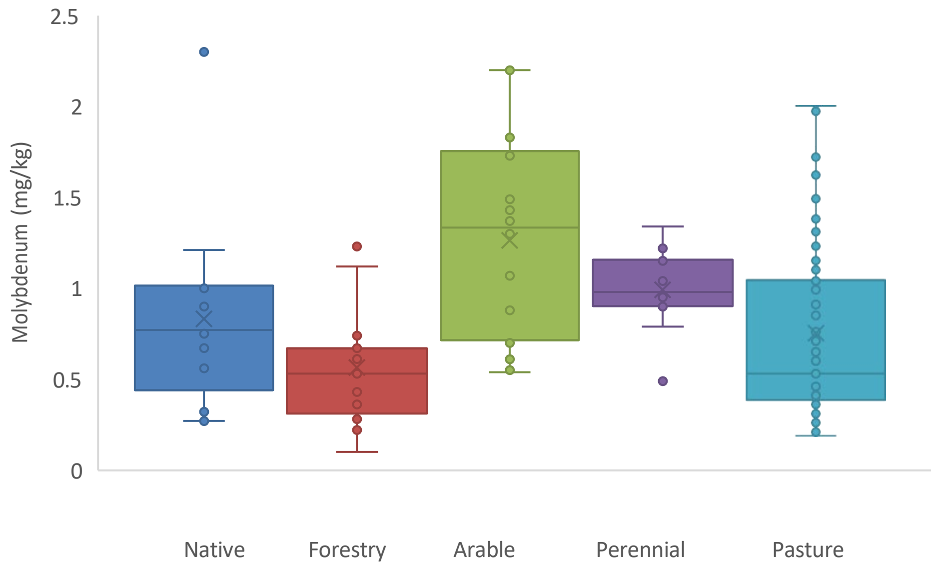

Figure 12. Boxpots of acid recoverable Mo (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Less known elements

Result for these elements are presented in Appendix 1 except for Tl and U, with highlights presented here.

Thallium

Perennial and arable land uses had significantly higher average Tl concentrations compared to native, pasture and forestry land uses (Figure 13). These results are consistent with the past use of Tl-containing pesticides on horticultural and arable land. However, natural Tl may adsorb onto clay minerals and iron oxides found in these soils (Zhuang et al. 2021; Lin et al. 2021).

Although average Tl concentrations were below the guideline value, individual sites under arable, perennial and a goat farm site receiving animal effluent exceeded the guideline for the

Protection of Environmental and Human Health (CCME 1999). Understanding if Tl is an emerging issue is desirable as is developing a New Zealand risk-based guideline. Thus, it is not clear if there are current diffuse sources of Tl to Waikato soils and further monitoring and research is required.

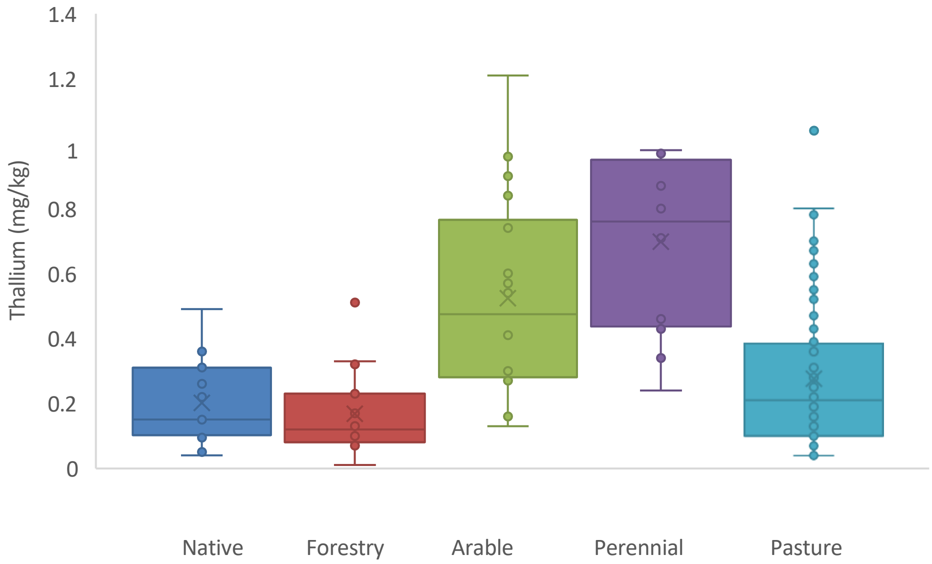

Figure 13. Boxpots of acid recoverable Tl (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Uranium

Fertilised land uses had elevated levels of U compared to native, consistent with accumulation of U impurities from P fertilisers (Figure 14). Historically, mineral P fertiliser used in NZ was derived from the ancient guano deposits, which contained relatively high U concentrations, about 60 mg/kg (Syers et al. 1986; Williams 1974; Menzel 1968; Trueman 1965). However, NZ currently buys its P rock on the world market and U concentrations measured more recently averaged 22.2 mg/kg (Taylor 2007). Nevertheless, shipments of Narau Island guano-derived phosphate rock were seen being unloaded in New Zealand in June 2024. An ongoing watch on U levels in fertilised soils is therefore needed.

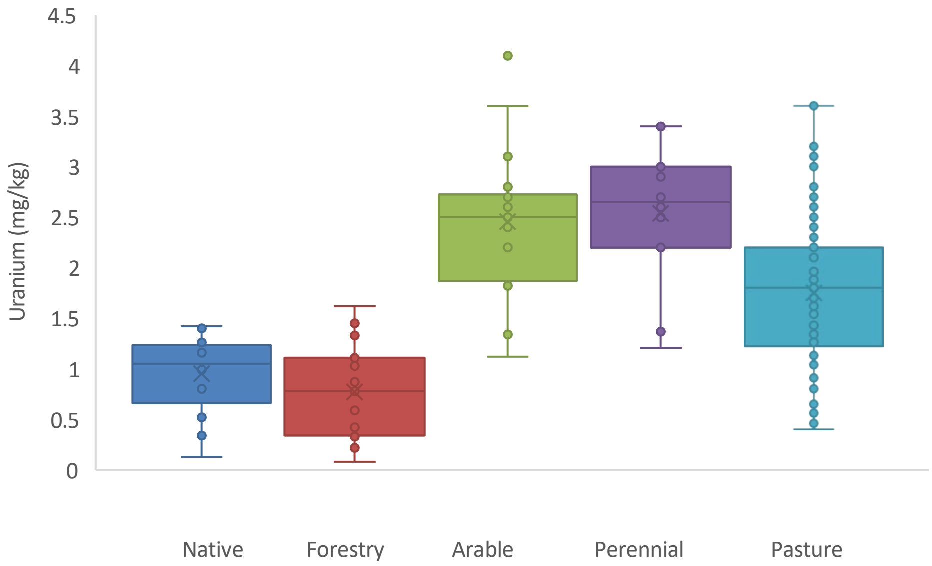

Figure 14. Boxpots of acid recoverable U (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

3.3 Trends 2001-2022

3.3.1 Introduction

Result highlights for elemental trends are presented in this section, while a more in-depth discussion of each element along with graphs is in Appendix 1. Results are presented in three groupings elements included in the National Environmental Standard for Soil Quality and Trace Elements, micronutrient elements, and the lesser-known elements.

3.3.2 Elements included in National Environmental Standard for Soil Quality and Trace Elements

Highlights

Arsenic

Results showed no significant ($p>0.05$) change in As for the overall data and in trend or pattern by soil order or land use. The lack of a trend indicates inputs of As are matching exports in production, losses in leaching, and in erosion while attached to soil particles.

Cadmium

Results showed no significant ($p>0.05$) change in Cd for the overall data and in trend or pattern by soil order or land use. The lack of a trend indicates that inputs and outputs of Cd are about in equilibrium. However, Cd is still applied as a contaminant in phosphate fertiliser, although at much lower quantities than in the past due to industry education, implementation of the New Zealand Cadmium Strategy and the tiered Fertiliser Management System resulting in fertilisers containing less Cd (CMG 2011, Gray and Cavanagh 2023). The Cd applied is being removed in produce or being leached lower in the soil profile. Consistent with the leaching of Cd, elevated Cd levels were identified in some groundwater bores in areas of intense farming (Hadfield 2011). However, the maximum level was still only ½ the drinking water standard for NZ of 0.00005 mg/L and well below the trigger value for freshwater protection for 95% of species of 0.0002 g/m^3, (ANZECC 2000). Taylor (2016) reported sediments in peat and riverine lakes and from the Firth of Thames, particularly at the mouth of the Piako River, showed considerable elevation, suggesting appreciable transfer of Cd from land to sediments.

Ongoing monitoring of Cd is important due to the risks to food production, human health and land use flexibility.

Chromium

Results showed a significant but slight nonlinear decreasing trend overall ($p=0.003$) but there were no significant ($p>0.05$) changes in trend or pattern for Cr by soil order or land use. Taylor (2016), using a mass balance approach, reported the loss of Cr from the top 10 cm of the soil and higher Cr in some lake and estuarine sediments consistent with transfer from land. Despite several known sources of Cr to soil in NZ, Cr appears to not be accumulating in soils of the Waikato region, but there may be some accumulation in lake and estuarine sediments.

Copper

Results showed a significant decreasing trend overall ($p=0.002$) but there were no significant ($p>0.05$) changes in trend or pattern for Cu by soil order. However, perennial and forestry land uses had a stronger curved trend, while other soil orders had a more linear trend. Several high-Cu sites were lost to urban sprawl or redeveloped as kiwifruit orchards, causing the average Cu concentration for perennial to fall. However, with the arrival of PSA, Cu use on kiwifruit blocks increased resulting in average Cu concentrations for perennial increasing again.

Monitoring of Cu should continue due to the number of sources of Cu and the current levels in soils. Advice should be provided to landholders where the soil guideline value for typical agricultural soils for the protection of ecological receptors for Cu is exceeded or where concentrations are below the potential deficiency level.

Fluorine
Results showed no significant trend overall ($p>0.05$). There were no significant ($p>0.05$) changes in trend or pattern for F by soil order or land use. The lack of risk-based toxicological guideline values limits understanding of environmental effects and the application of management options. Monitoring of F should continue due to the potential risks to animals, humans and the environment from legacy F and the continuing application of F in mineral phosphate fertiliser. Further research into the ecotoxicity of F to inform soil guideline values should be encouraged.

Lead
Results showed no significant trend overall ($p>0.05$). There were no significant ($p>0.05$) changes in trend or pattern for Pb by soil order or land use indicating inputs and outputs are about equal. However, the use of Pb has decreased significantly since the 1980's, with the phasing out of Pb in roof flashing, petrol, paint, bullets, metal can solder, plumbing, pesticides and batteries (Tchounwou et al. 2012; Kabata-Pendias & Mukherjee 2007; Gaw 2006). Nevertheless, legacy Pb can be a major source of Pb exposure (Martin et al. 2023; Laidlaw et al. 2014) and Pb is still used in many products, such as brass or chrome tap fittings, aviation gas, electronics, fishing gear and tyre balance weights (Levin et al. 2021; Taylor & Kruger 2020).

Monitoring of Pb should continue due to applications continuing from current sources, potential issues with legacy Pb, and due to the potential toxicity of Pb to humans and the environment.

Nickel
Results showed there was a significant increasing nonlinear trend overall ($p=0.019$) but there were no significant ($p>0.05$) changes in trend or pattern for Ni by soil order or land use. Generalised fertiliser use is a possible driver of increases in Ni (Taylor 2016). Nevertheless, there are no current issues apparent with Ni in the Waikato region.

Zinc
Results showed no significant trend overall ($p>0.05$), in trend or pattern for Pb by soil order or land use. However,

3.3.3 Micronutrient Elements

Highlights
Results showed no trends for B with little of concern for the region.

As about a quarter of sites measured in the region have low Co concentrations where deficiency can occur (<2mg/kg, Hawke et al. 1994), so stock supplements and Co-boosted fertilisers are commonly used to manage bush sickness However, there is no evidence of accumulation of Co in soil in the Waikato region and no trends with land use or soil order were identified. Thus, Co appears stable with no clear impact on soil of animal supplementation with Co, despites decades of animal supplementation.

The mixed modelling results showed there was a significant declining nonlinear trend for Mo, both overall ($p=0.004$, Figure 42) and by soil order ($p=0.001$, Figure 43). A decline in Mo combined with increases in Cu may result in Cu toxicity or molybdenosis for farm animals, plants and even humans (Ward 1994).

3.3.4 Less Known Elements

Highlights

Results showed inconsistent trends for these elements.

4 Conclusions

Monitoring is providing information on the current trace element state and trend in soils of the Waikato region.

Significantly ($p<0.05$) elevated levels of As, Cd, Cr, Cu, F, Pb, Ni, Zn, Co, Sb, Hg, Ag, Tl and U were found for arable, perennial and pasture compared to native. Some trace elements (As, Cd, Cu, Tl, Zn) were found to be near or above the New Zealand Soil Contaminant Standards using the rural residential scenario guideline values and/or the protection of ecological receptors for non-food production and agricultural land. Of these, Cd is currently of greatest concern within the Waikato region due to the extent of Cd accumulation in soil, the risk of exceeding food standards for some crops and animal products, potential restriction on land use and farm production, and contamination of the wider environment including soil, surface and ground waters, estuaries and lakes. Waikato regional council should continue to support and maintain membership of the Cadmium Management Group to provide leadership for managing Cd.

Other trace elements (Co, Cu, Mo, Zn) are at or close to levels where deficiency could occur at some sites. These are usually well known for productive land uses with management techniques available to overcome deficiencies. Cu and Zn are remarkable as they can be an issue from excess due to contamination, as well as deficiency due to naturally low Cu or Zn contents for specific soil types.

Advice should be provided to landholders where the soil guideline values are exceeded, or trace element concentrations are at or close to levels where deficiency could occur.

There are some trace elements (F, U) for which there is limited information on their environmental effects, e.g. despite the high ranking of F in priority listings and the occurrence of animal health issues, there is no accepted guideline value for total F in soil, although Cronin (2000) and Cavanagh (2019) have provided indicative guidelines based on limited data. Similarly, chemical toxicity guideline values for U are lacking as current guideline values are based on radioactivity. Further research into the ecotoxicity of F and U to inform risk-based soil guideline values should be encouraged.

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5 Appendix 1. Additional detail and graphs of trace elements monitored

Arsenic (As)

Arsenic is a naturally occurring element commonly found in soils at trace levels. As it is chemically like P, an essential element, it can be assimilated by biota by the same mechanisms. Thus, it can be toxic to animals, including humans and is also a carcinogen, associated with lung and skin cancers (Robinson et al. 2004). The greatest risk to people posed by As in the Waikato region is if it gets into drinking water or food. New Zealand Food Safety Haumaru Kai Aotearoa of the Ministry of Primary Industries indicates Foods with high levels of inorganic arsenic can be found in watercress grown near the Waikato River and in geothermal areas (MPI 2020).

Arsenic has a wide range of industrial and agricultural sources, as well as natural sources, including As based pesticides, copper-chrome-arsenic (CCA) treated timber, volcanic material, geothermal discharges, coal and As-minerals. Agricultural chemicals include insecticides, herbicides, fungicides, algicides, sheep dips, wood preservatives, and dyestuffs (Tchounwou et al. 2012). The most common current sources in the Waikato region are geothermal, both natural and discharges from geothermal power stations, and CCA-treated timber. Note that As is no longer used in agricultural chemicals in New Zealand.

The New Zealand Soil Contaminant Standard for As using the rural residential scenario is 17 mg/kg (MfE, 2011), while the Guideline value for the Protection of Ecological Receptors for non-food production and agricultural land uses (Cavanagh 2019) is 20 mg/kg. In comparison, the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health for As in agricultural soil (CCME 1999) is 12 mg/kg.

The mixed modelling results showed no significant ($p>0.05$) change in As for the overall data (Figure 15) and there were no significant ($p>0.05$) changes in trend or pattern for As by soil order (Figure 16) or land use (Figure 17). The lack of a trend indicates inputs of As are matching exports in production, losses in leaching, and in erosion while attached to soil particles. It is likely that current inputs of As are low and concurrent losses through exports in production, losses in leaching, and in erosion are minimal.

Nevertheless, there were significant differences between soil orders ($P<0.01$) and land uses ($p<0.01$) but not interactive between soil order and land use ($p=0.99$). Granular soils had consistently higher average As concentrations than other soils, while Pumice, Podzols and Organic soils had consistently lower average As concentrations. Granular soils have high concentrations of iron minerals, while Pumice, Podzols and Organic soils have lower concentrations of iron minerals, compared to other soils. Arsenic adsorbs mainly to amorphous iron oxyhydroxides with redox, pH and the presence of other potential competitive sorbents, such as organic acids, also being important factors (Bowell 1994). Thus, As is readily sorbed in Granular soils regardless of its source.

Soils under perennial land use also had consistently higher average As concentrations than other land uses although these soils were rarely Granular soils. Assuming native land use approximates background values, i.e. as if the soil was unimpacted by human activities, perennial soils again have considerably higher average As concentrations compared to other land uses for both calculated and measured values (Figures 8-9). There are many potential As sources associated with horticultural land including CCA-treated posts and the past use of As-containing pesticides like lead arsenate and monosodium methanearsonate (MSMA). Fortunately, As-containing pesticides are no longer used in New Zealand, but the higher levels of As in horticultural land maybe evidence of leaching from CCA treated framing or legacy As from past use of As-containing pesticides.

Consistent with the mixed modelling trend results, the current state of As in Waikato soils in 2020 presented in Figure 2 showed sites under native, forestry and pasture had similar median and quartile values indicating As is not accumulating in the soil in these land uses. However, sites under cropping and perennial land uses had elevated As compared with sites under native.

The 5-yearly rolling average concentrations of major land uses were all below the Soil Guideline Values Protective of Human Health and for the protection of ecological receptors (Figure 18). However, two individual sites exceeded the New Zealand Soil Contaminant Standards using the rural residential scenario (25% of produce consumed is home-grown) value. One was a very long- term apple orchard research station, likely to have received considerable amounts of As-containing pesticides, and the other was a low-lying dairy pasture that was periodically flooded by the Waikato River, which contains As from natural geothermal discharges and discharges from geothermal power stations.

Although there is no current increasing trend in As in perennial soils or other soils of the region, monitoring should continue due to the toxicity of As and the presence of concentrations near or above the guideline values for human health and the protection of ecological receptors. Replacements for As in timber treatment and in dyes should be encouraged.

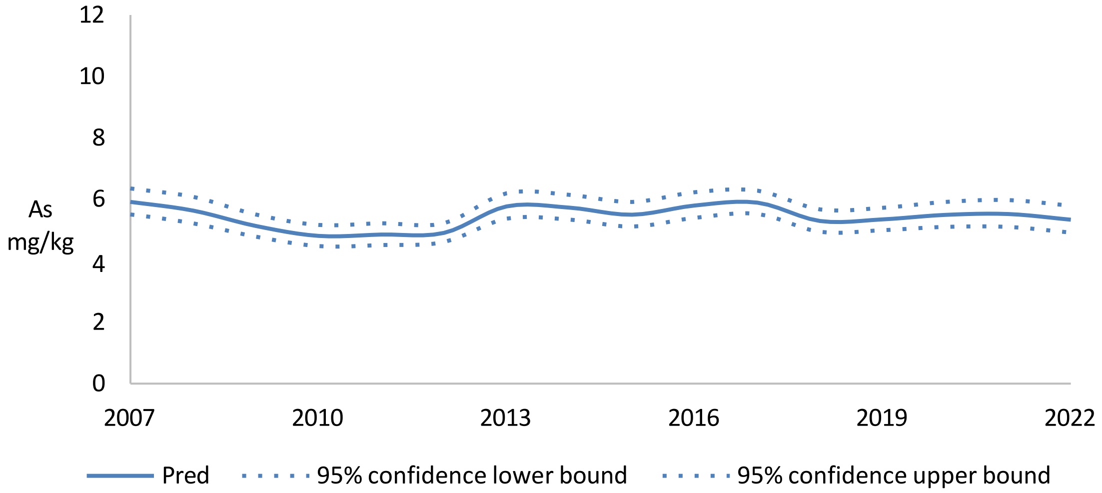

Figure 15. Change in mixed modelling average As concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

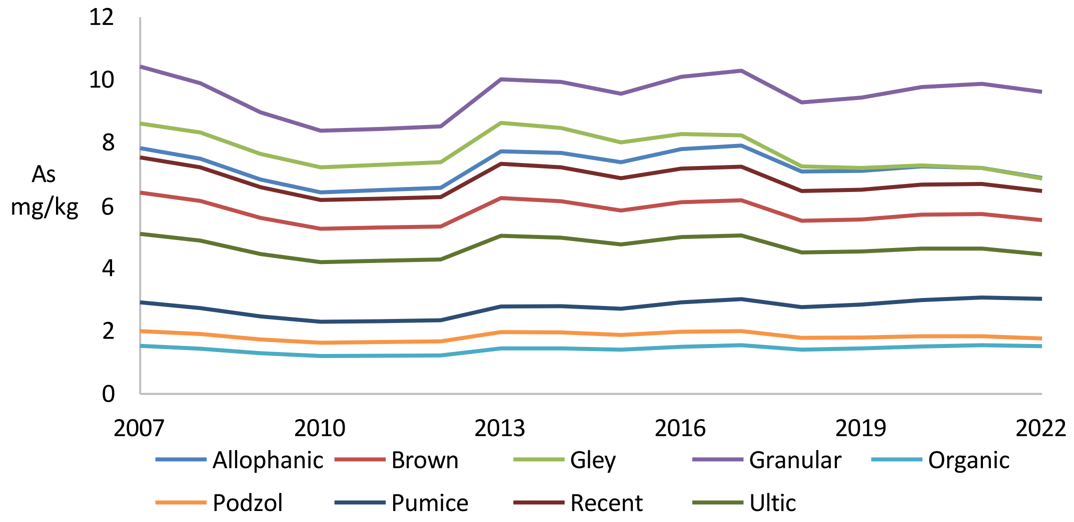

Figure 16. Change in mixed modelling average As 2007-2022 by soil order.

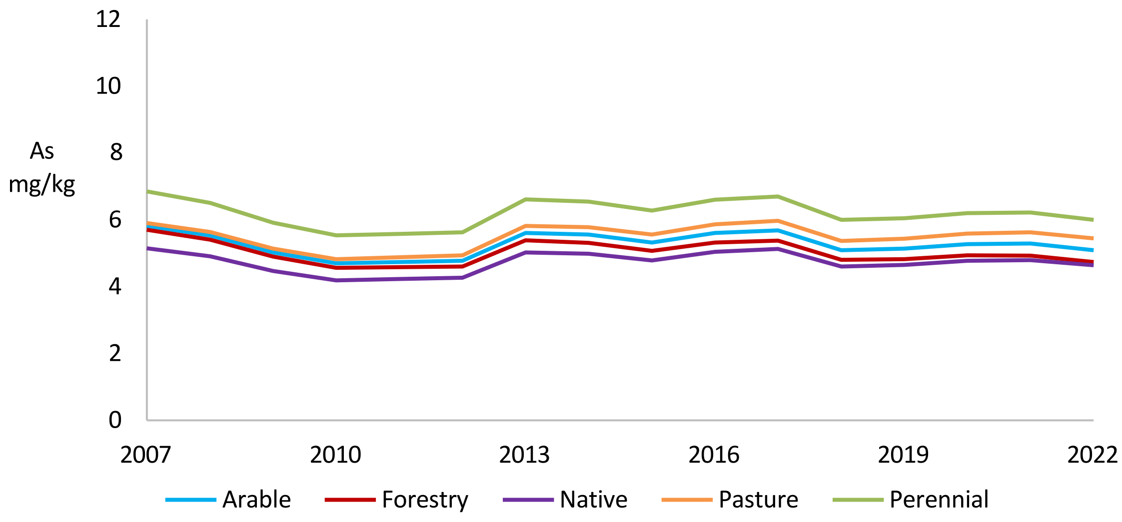

Figure 17. Change in mixed modelling average As 20017-2022 by land use. The New Zealand Soil Contaminant Standard using the rural residential scenario is 17 mg/kg (MfE, 2011).

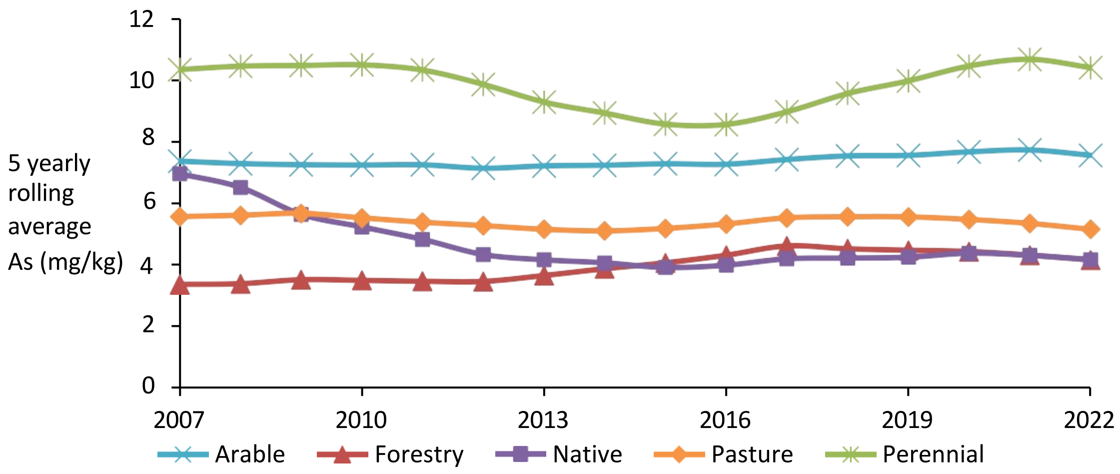

Figure 18. Average As by land use 2007-2022. The New Zealand Soil Contaminant Standard using the rural residential scenario is 17 mg/kg (MfE, 2011).

Cadmium (Cd)

Cadmium is considered a priority contaminant in New Zealand (MfE 2011). It is a human and ecological health issue that may suppress animal and microbiological life, impact human health, while excessive levels of Cd in soils can restrict land use flexibility (CWG 2008). Although Cadmium (Cd) is a heavy metal that occurs naturally in soils at trace levels, it is also a trace contaminant in mineral phosphate fertilisers. The use of phosphate fertilisers over long timeframes in New Zealand has led to a gradual accumulation of Cd in fertilised soils, where it is predominately bound to minerals and organic matter in the topsoil (CWG 2008; Roberts et al. 1994). The Waikato and Taranaki regions have the highest Cd concentrations reported in New Zealand (Cavanagh 2014; CWG 2008).

Major sources of Cd overseas include mining and smelting and the products and waste produced, plating, battery production, pigment production, plastic stabiliser production. Livestock manure also contains Cd and high cumulative loadings of manure can be an important source over time. Cd also finds its way from these sources and into biosolids, although recent regulation and industrial treatment has reduced levels in biosolids considerably (Chaney 2010).

Other minor sources of Cd in the Waikato area are nickel-cadmium batteries and other electrical waste, Cd impurities in Zn coatings used on metal structures (these elements are usually co-contaminants), while cigarette smoke is one of the highest sources of cadmium exposure for smokers.

Once it is accumulated in soil, depletion of Cd occurs slowly by plant uptake, removal in livestock, leaching and erosion (Schipper et al. 2011; McDowell 2010; Gray et al. 2003; Loganathan & Hedley 1997). High levels in soils increase the risk that Cd will enter the human food chain and eating Cd-containing foods is the major pathway for most human exposure (CWG 2008; WHO 1992). Some plants, such as potatoes, wheat, and green leafy vegetables, can take up Cd in excess of food standards. Excessive levels of Cd in food can have implications for human health and excessive levels of Cd in soils can restrict land use flexibility (CWG 2008).

Earlier SoE monitoring of Cd, led by WRC, highlighted the potential health and environmental issues associated with this element (Kim 2005) and led to the formation of the New Zealand Cadmium Working Group to develop a management strategy for Cd (CWG 2008). Key parts of the strategy are soil monitoring and using the Tiered Fertiliser Management System to manage the rates and choice of phosphate fertiliser. In response to concerns about Cd in the New Zealand environment, the fertiliser industry introduced voluntary limits on Cd levels in phosphate fertilisers in the mid 1990's System (CMG 2011, Gray and Cavanagh 2023). The fertiliser industry is now an active participant in the Cadmium Management Group, implementing the Cadmium Strategy, and reporting annually on Cd concentrations in current fertilisers.

The New Zealand Soil Contaminant Standard using the rural residential scenario is 0.8 mg/kg (MfE, 2011), while the Guideline value for the Protection of Ecological Receptors for non-food production and agricultural land uses (Cavanagh 2019) is 1.5 mg/kg. In comparison, the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health for Cd in agricultural soil (CCME 1999) is 1.4 mg/kg. Similar values are used in the Tiered Fertiliser Management System. Where Cd is < 0.6 mg /kg, the soil is within background levels. There are three tiers with increasingly stringent restrictions on the choice and rate of phosphate fertiliser as soil cadmium increases 0.6-1.8 mg Cd/kg and the highest tier, where Cd >1.8 mg/kg, beyond which there should be no further net accumulation.

About a quarter of sites measured, including arable, horticultural and pastoral sites, had Cd concentrations exceeding the New Zealand the New Zealand Soil Contaminant Standards using the rural residential scenario and 1 % of sites (intensive long-term dairy and kiwifruit orchards) exceeded both the soil Guideline Values Protective of Human Health and ecological receptors. These results reflect the long-term nature of Cd contamination, the history of large applications of Cd-containing fertilisers in the region and the concerns already raised by Waikato Regional Council at the national level (Kim 2005).

The mixed modelling results showed no significant ($p>0.05$) change in average Cd for the overall data (Figure 19) and there were no significant ($p>0.05$) changes in trend or pattern for Cd by soil order (Figure 20) or land use (Figure 21). Nevertheless, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Allophanic and Granular soils had higher average Cd concentrations than other soil orders, while Podzol Pumice and Ultic soils had lower average concentrations. Both mixed modelling and measured 5-yearly rolling average showed perennial, arable and pasture have Cd concentrations well above native (Figures 21-22.

Intensive perennial and dairy farming are prominent land uses on Allophanic and Granular soils and it is likely that land management with the application of large quantities of Cd-containing phosphate fertiliser, is overriding any soil order effects. In particular, Taylor (2016), while investigating the fate of trace elements impurities in fertilisers, found the highest median Cd concentration in soil was in kiwifruit orchards, which are a high intensity crop so receive high P fertiliser inputs, e.g. applications of 1 t/ha superphosphate of reactive rock phosphate (RRP) +

mixtures of "organic inputs" were recorded at some of these sites. The large applications of RRP to organically farmed kiwifruit and corresponding elevation in soil Cd concentrations may be of particular concern to organic kiwifruit growers.

Transfer of Cd to other environmental compartments has also been reported in the Waikato region. Consistent with the leaching of Cd, elevated Cd levels were identified in some groundwater bores in areas of intense farming (Hadfield 2011). However, the maximum level was still only ½ the drinking water standard for NZ of 0.00005 mg/L (USEPA 2004) and well below the trigger value for freshwater protection for 95% of species is 0.0002 g/m^3, (ANZECC 2000). In comparison, Taylor (2016) showed Cd in surface water was below detection in nearly all samples. There is currently minimum risk to human and animal health from Cd in drinking water, but this assessment will need revision if levels in groundwater increase.

Taylor (2016) also reported sediments in peat and riverine lakes and from the Firth of Thames, particularly at the mouth of the Piako River, showed considerable elevation, suggesting appreciable transfer of Cd from land to sediments. The accumulation of Cd in sediment may be considered a potential source of Cd. Some management activities, in particular dredging, may release Cd (and other metals) back into the water column. Impacts on the marine environment, such as high uptake of anthropogenic Cd by plankton communities have been reported (Auger et al. 2015). Thus, consideration of environmental effects is needed by water managers before carrying out activities that may significantly increase the release contaminants from sediments back into water.

If accumulation of Cd continues, food standards for some crops and animal products are likely to be exceeded, restricting land use and farm production, and resulting in contamination of the wider environment; soil, surface and ground waters, and restricted aquatic environments, e.g. estuaries and lakes. However, except for horticultural soils, Cd soil content seems to have plateaued with inputs of Cd equalling losses in produce and leaching. The transfer of Cd to the water domain is a potential issue for regional councils. Monitoring of Cd should continue due to the number of sites exceeding guideline values and the risks to human health and land use flexibility. Advice should be provided to landholders where the soil guideline values are exceeded. Membership of the Cadmium Management Group should be maintained and active.

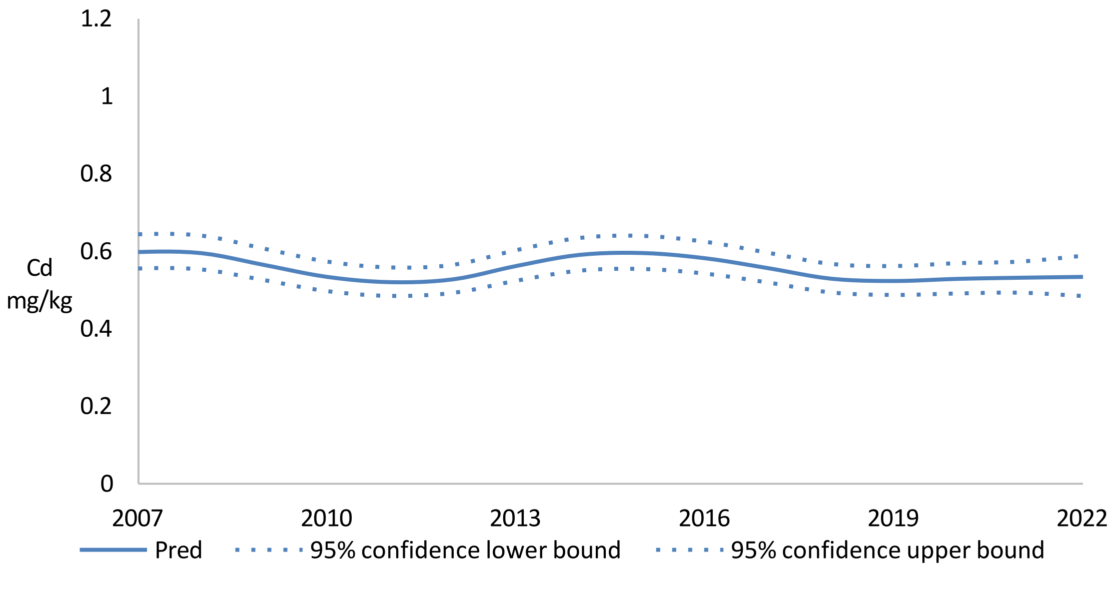

Figure 19. Change in mixed modelling average Cd concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

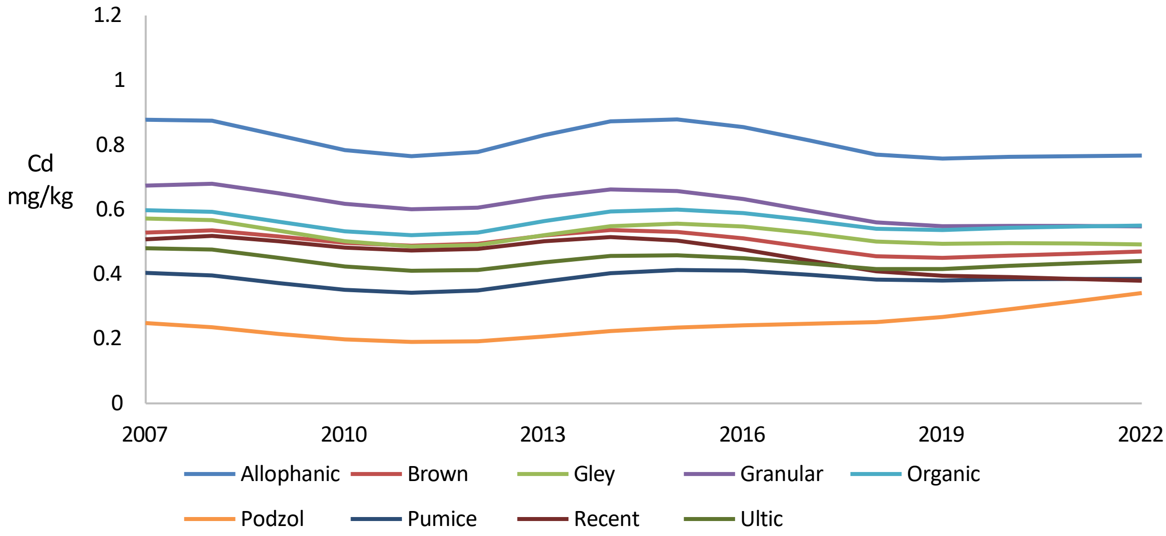

Figure 20. Change in mixed modelling average Cd 2007-2022 by soil order.

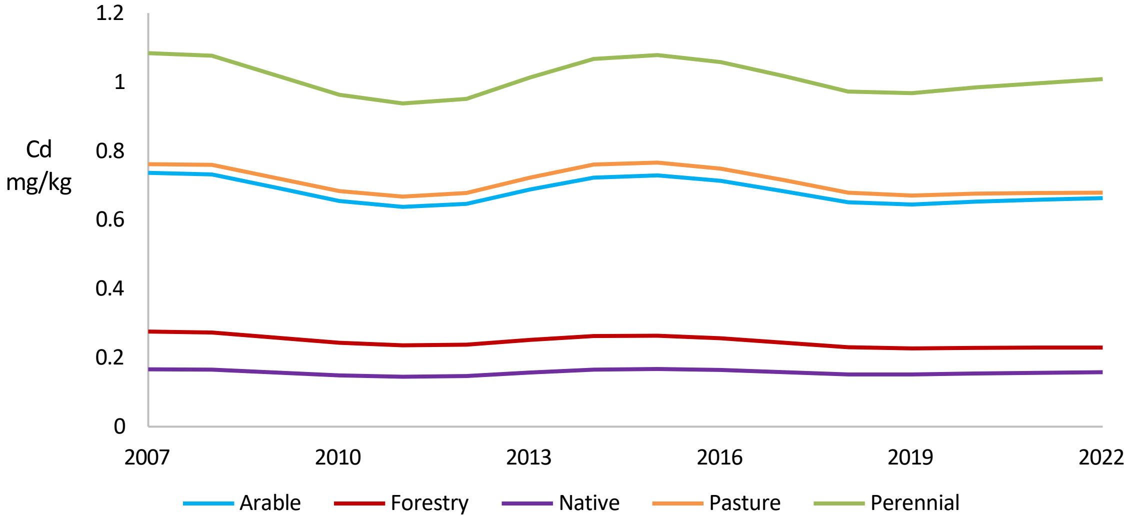

Figure 21. Change in mixed modelling average Cd 2007-2022 by land use.

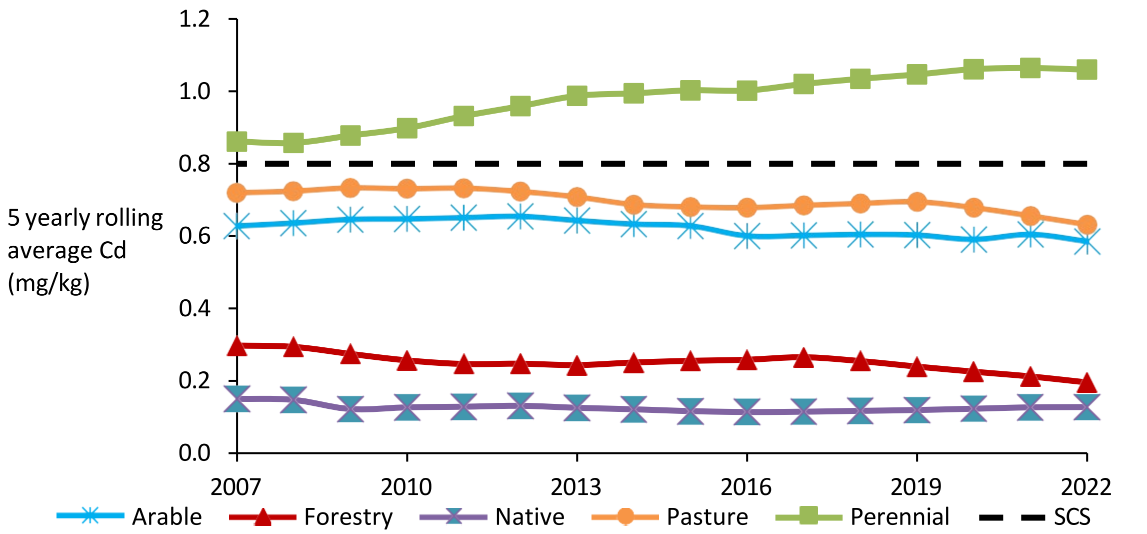

Figure 22. Average Cd by land use 2007-2022. The soil guideline value for agricultural soils for the protection of ecological receptors for Cd is 1.5 mg/kg (Cavanagh 2019), while the New Zealand Soil Contaminant Standards using the rural residential scenario is 0.8 mg/kg (MfE, 2011).

Chromium (Cr)
Chromium is essential for animals and needed by the human body in small amounts for insulin action and the metabolism of proteins and carbohydrates but it has a varying toxicity depending on its valency and speciation in the environment, with Cr(VI) being much more toxic than Cr(III) (Ma & Hooda 2010; Salminen et al. 2005). Soluble Cr(III) is considered relatively harmless at levels normally encountered, but Cr(VI) is highly toxic because it bears a structural similarity to S(VI), causing liver and kidney damage and acting as a carcinogen (Ma & Hooda 2010; Salminen et al. 2005). The greatest risk to people posed by Cr in the Waikato region is if it gets into drinking water or food.

The New Zealand Soil Contaminant Standards using the rural residential scenario for Cr (VI) is 290 mg/kg (MfE 2011), while it is 300 mg/kg for the protection of ecological receptors (Cavanagh 2019). All sites had Cr concentrations below these guideline values. In comparison, the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health for total Cr in agricultural soil (CCME 1999) is 64 mg/kg, clearly much lower than the New Zealand Soil Contaminant Standards using the rural residential scenario (25% of produce consumed is home-grown).

Total Cr measures both Cr(III) and Cr(VI) but the Canadian guideline for total Cr is intended to be protective where Cr(III) predominates (CCME 1996). Generally speaking, in most cases it is safe to assume that most Cr(III) in soil will remain as Cr(III). Additionally, soil organic matter will reduce Cr(VI) to Cr(III) and inhibit the reverse process under nearly all soil conditions (Kabata-Pendias and Pendias, 2001; Chaney et al. 1997; McGrath, 1995). However, Mn oxides in soil can enhance oxidation of Cr(III) to Cr(VI) under alkaline conditions (Avudainayagam et al. 2003). Fortunately, soils of the Waikato region are naturally slightly acidic and usually have high organic matter, so favouring formation of Cr(III).

Major sources of Cr include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production (Tchounwou et al. 2012). Chromium is extensively used as a timber preservative (CCA) in the Waikato region, and across NZ (Carey et al. 1996). Soils surrounding CCA treated timber have significantly higher Cr concentrations than control soils (Robinson et al. 2006). Chromium has also been found as an impurity in phosphate fertiliser (Taylor 2016). However, sources of Cr emissions in NZ are few and the reported average atmospheric Cr deposition flux for NZ is 2.8 mg/m^2/y (Gray et al. 2003). The deposited Cr is subject to adsorption or precipitation reactions, uptake by plants, and, under favourable soil pH and moisture conditions, leaching to subsurface layers.

The mixed modelling results showed a significant nonlinear trend overall ($p=0.003$, Figure 23) and there were no significant ($p>0.05$) changes in trend or pattern for Cr by soil order (Figure 24) or land use (Figure 25). Nevertheless, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Mixed modelling soil order differences show Granular soils had considerably higher average Cr concentrations compared with the next highest soil orders (Brown and Gley soils). Granular soils have high concentrations of iron minerals that can form Cr minerals. Taylor (2016), while investigating the fate of trace elements found in fertilisers, used PCA to show Cr was associated with Fe, Ni and V. Similar strong correlation between Cr and Ni was also reported in Salminen et al. (2005). Also, Ma and Hooda (2010) reported lithogenic Cr was generally associated with Fe, while anthropogenic Cr was generally associated with organic carbon. These studies suggest the Cr in Granular soils is lithogenic, i.e. natural.

Mixed modelling showed perennial had higher average concentrations of Cr than other land uses, although this differed from the measured the 5-year rolling average where perennial average Cr concentrations were like other land uses and arable average had higher concentrations of Cr than other land uses (Figures 25 - 26). Investigating individual sites, the higher concentrations of Cr in arable soils were nearly all on Granular soils, thus most of the Cr at these sites is likely natural. However, sites in perennial with higher concentrations compared to other land uses were on Allophanic or Brown soils and anthropogenic sources may be contributing Cr to these horticultural sites.

Possible anthropogenic sources of Cr in horticultural soils are impurities in fertiliser and CCA treated timber used as posts and framing. Soils in the Waikato region tend to be slightly acidic and so applied Cr is expected to remain as Cr (III). Cr(III) is nearly immobile when bound to soil by adsorption or precipitation, especially under moderately oxidising and reducing conditions and near-neutral pH values (Ma & Hooda 2010; Salminen et al. 2005). This limits Cr entry into the food chain and leaching to groundwater. However, Taylor (2016), using a mass balance approach, reported the loss of Cr from the top 10 cm of the soil, consistent with leaching, although Cr was below or at the detection limit when measured in surface and groundwater samples. This behaviour was explained by chelation, oxidation and remobilisation of Cr(III) to Cr(VI) under near neutral soil pH along with the remobilisation and precipitation of iron. The Cr(VI) could leach down the soil profile until it was reduced to Cr(III) again deeper in the soil. Taylor (2016) also showed Cr to be higher in dune lake and Firth of Thames sediments compared with West Coast sediments, consistent with Cr transport.

There also appears to be element-specific chemical barriers that limited the plant transfer of some potentially toxic elements from soil to plants, including Cr, e.g. Cr exhibits a low potential for plant absorption compared with Cd, Cu, Ni, and Zn under the same conditions (Chen et al. 2010). Thus, accumulation of Cr in food appears to not be of concern.

Overall, despite several known sources of Cr to soil in NZ (the atmospheric deposition flux, fertilisers, treated timber), Cr is not accumulating in soils of the Waikato region and there appears little, if any, evidence of anthropogenic Cr accumulating in other environmental compartments, e.g. sediment.

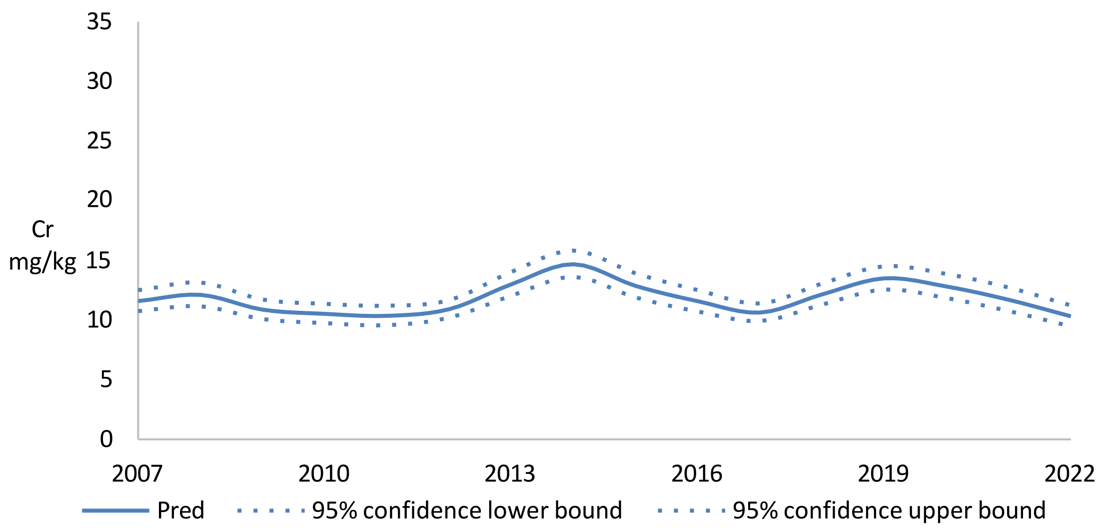

Figure 23. Change in mixed modelling average Cr concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

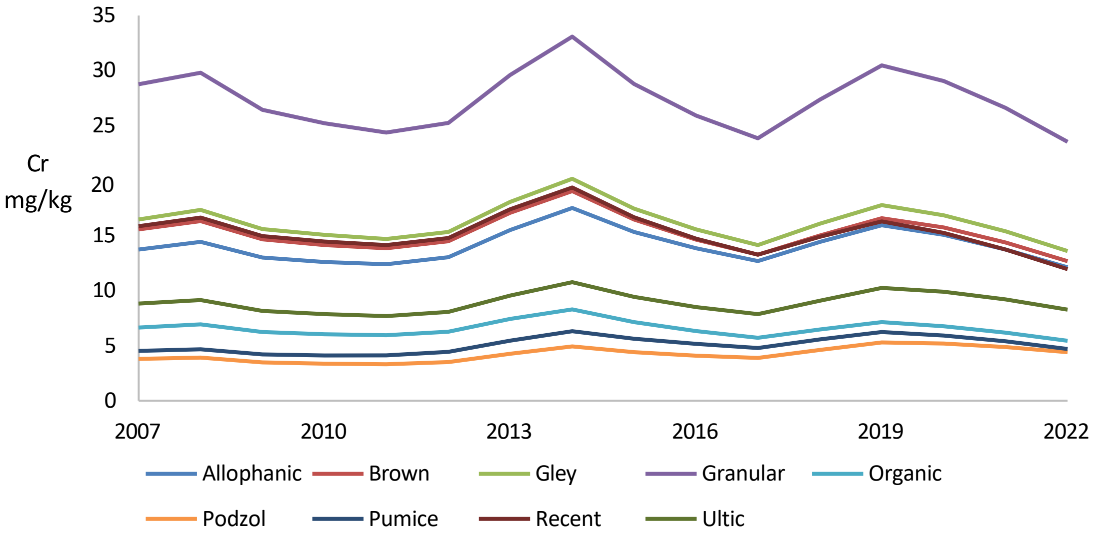

Figure 24. Change in mixed modelling average Cr 2007-2022 by soil order.

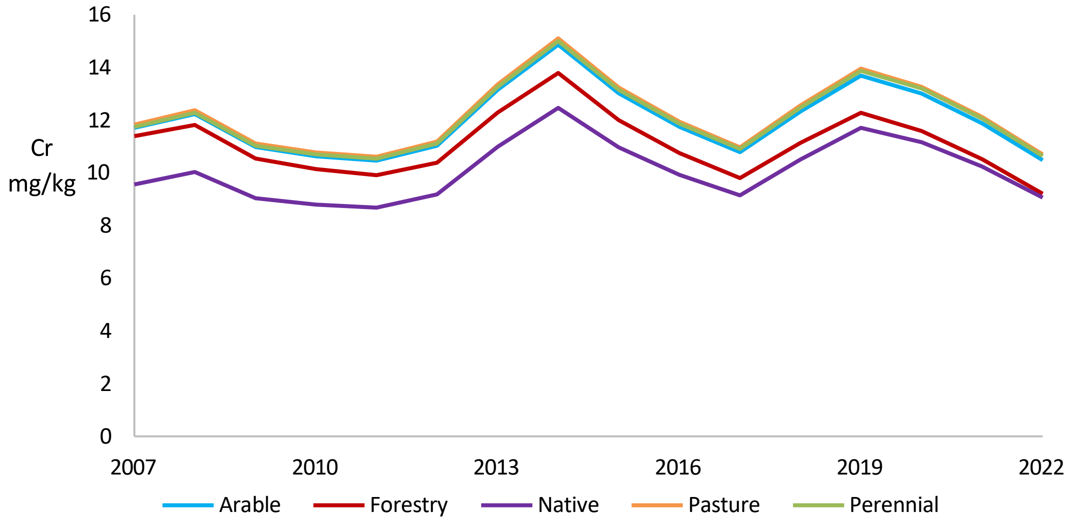

Figure 25. Change in mixed modelling average Cr 2007-2022 by land use.

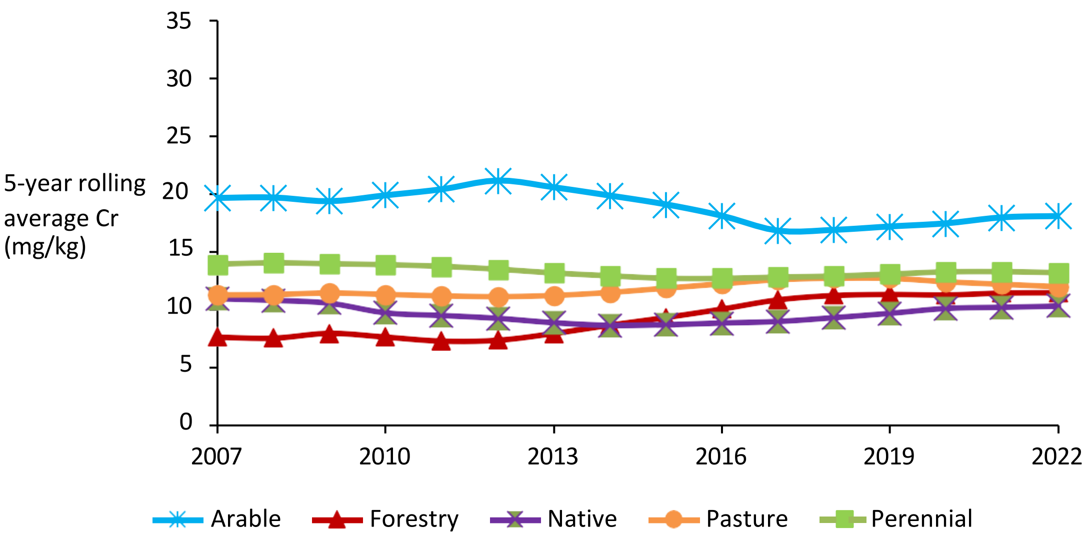

Figure 26. Average Cr by land use 2007-2022. The soil guideline value for agricultural soils for the protection of ecological receptors for Cr is 300 mg/kg (Cavanagh 2019), while the New

Zealand Soil Contaminant Standards using the rural residential scenario is 290 mg/kg (MfE, 2011).

Copper (Cu)

Cu is essential for the growth and development of higher plants, terrestrial mammals, aquatic organisms and some algae, but may become toxic at higher concentrations and is considered a priority contaminant by NZ resource managers (MfE 2011). Accumulation of Cu in soil is considered relatively safe for human health but of risk to animal and ecological health as it increases baseline dietary uptake of animals from plants and direct ingestion of soil. There are multiple sources of Cu in the Waikato region including many agricultural and horticultural chemicals, impurities in fertilisers, timber treatment chemicals, copper piping and guttering, and vehicle brake linings.

Conversely to toxicity, Cu deficiency in crops is widespread and often not recognised. Alloway (2008a) stated this undetected form of Cu deficiency in crop plants is the most ubiquitous and economically important, e.g. 25% of soils in Germany have Cu concentrations that can result in Cu deficiency in sensitive crops such as cereals, spinach and lucerne (Kabata-Pendias & Pendias 2001). Cu deficiency may be an issue for unfertilised soils in the Waikato region due to their high organic content binding available Cu, and for sensitive crops if arable farming increases, but normal farming practices for dairy, sheep and beef, make deficiency unlikely for animals. Alloway (2008a) suggested concentrations <5 mg/kg could indicate deficiency.

Although Cu toxicity in animals has been reported if Mo intake is too low (Section 3.12), Cu toxicity has also occurred where dairy cows have been dosed with Cu to avoid deficiency but then fed palm kernel as a supplementary feed product. Palm kernel, which can have high concentrations of Cu, combined with the direct Cu dose, induced copper toxicity (Dias 2010).

The upper limit for Cu in soil set by the Soil Contaminant Standard using the rural residential scenario is 10,000 mg/kg (MfE, 2011) is 10,000 mg/kg. However, the Guideline values for the Protection of Ecological Receptors for non-food production and agricultural land uses (Cavanagh 2019) are 55 and 110 mg/kg, respectively. International risk-based guideline values were also assessed as there is a large difference between human and ecological guidance values. Of these, the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health for copper in agricultural soil (CCME 1999) was identified as the nearest risk-based match to local environmental conditions. The guideline value is 63 mg/kg. The mixed modelling results showed a significant decreasing trend overall ($p=0.002$, Figure 27). There were no significant ($p>0.05$) changes in trend or pattern for Cu by soil order (Figure 28). However, there were significant differences in the trend pattern for land use and between land uses ($p<0.01$, Figure 29) and soil orders ($P<0.01$, Figure 28). The horticultural and forestry land uses had a stronger curved trend, while other soil orders had a more linear trend.

There was also a strong curve in the 5-yearly rolling average trend for horticultural soils (Figure 30). Initial sites, in 2001, included long-term vineyard, apple and berry orchards that had historically high applications of Cu fungicides. Six samples (about 1% of samples) from long-established apple orchards exceeded the soil guideline value for typical agricultural soils for the protection of ecological receptors for Cu of 110 mg/kg (Cavanagh 2019) but all sites had Cu levels well below the New Zealand Soil Contaminant Standards using the rural residential scenario of 10,000 mg/kg. Several of high-Cu sites were lost to urban sprawl or redeveloped as kiwifruit orchards. This caused the average Cu concentration for perennial to fall. However, with the arrival of PSA, Cu use on kiwifruit blocks increased resulting in average Cu concentrations for perennial increasing again (Figure 24). Nevertheless, only one apple orchard currently exceeds the soil guideline value.

Sixteen Native, forestry and a pastoral site (about 3 %) had Cu concentrations below the level at which Cu deficiency could occur. However, only the pastoral site would likely be affected, and farming practices would mean these animals are likely receiving Cu supplements.

Mixed modelling also showed Allophanic and Granular soil orders had had higher average concentrations compared to other soil orders (Figure 28). This result was surprising for Allophanic soils as natural Cu concentrations decrease with increasing silica content of the soil especially for soils containing allophane and/or derived from rhyolitic ash (Neall 2009; Kobayashi and Shoji 1976). Soil in horticultural land use had 2-3 times the concentration of Cu compared with other land uses (Figures 28-29). Intensive perennial is a prominent land use on Allophanic and Granular soils and it is likely that land management with the application of large quantities of Cu-based agrichemicals, is overriding any natural soil effects. Cu concentrations for other land uses are similar to native levels and trends are near flat suggesting Cu accumulation is not accumulating in these soils at present.

Where inputs of Cu exceed losses in production, there is potential for Cu to transfer to other environmental compartments. Leaching of Cu from agricultural land can be an important source of surface and ground water contamination (Richardson et al. 2015). The mobility of Cu is especially tied to that of SOM, e.g. if the SOM is immobile, so is Cu complexed with it. However, the DOM fraction of SOM is mobile and has a great affinity for Cu, thus inhibits its sorption onto the soil matrix. Cu concentrations in soil extractions were found to be inversely related to SOM (McGrath et al. 1988), while the most common form of Cu found in soil pore water was complexed and strongly correlated with DOM (Hough 2010; Linde et al. 2007; Berggren 1992). In the Waikato region, highest concentrations were in Lake Ngaroto, a peat lake, consistent with movement of Cu in DOM from peatland to the lake (Taylor 2016). The Cu trigger value for freshwater protection for 95% of species is 0.0014 g/m^3 (ANZECC 2000) was exceeded in about half the samples taken from this lake. However, only one sample exceeded the trigger value for 90% protection (0.0018 g/m^3).

Accumulation of Cu in agricultural soils is a source of contamination to shallow groundwater and surface water in the Netherlands (Schipper et al. 2008), thus the highest leaching rates in the Waikato region could be expected from wet Gley soils and peaty Organic soils and in agricultural regions with intensive horizontal drainage systems. However, Cu in Waikato River samples were below detection until the river received urban inputs from Hamilton City, which was attributed to this city's discharge of stormwater (Taylor 2016). Also, a large contribution of Cu came from the Waipa River. A large proportion of the soils in the Waipa River catchment are fine particles derived from sedimentary material and the sediment load of this river is much higher than that in the Waikato River, suggesting particle transfer from erosion as a transport mechanism for Cu as well as transport in DOC.

Monitoring of Cu should continue due to the number of sources of Cu and the current levels in soils. Advice should be provided to landholders where the soil guideline value for typical agricultural soils for the protection of ecological receptors for Cu is exceeded or where concentrations are below the potential deficiency level.

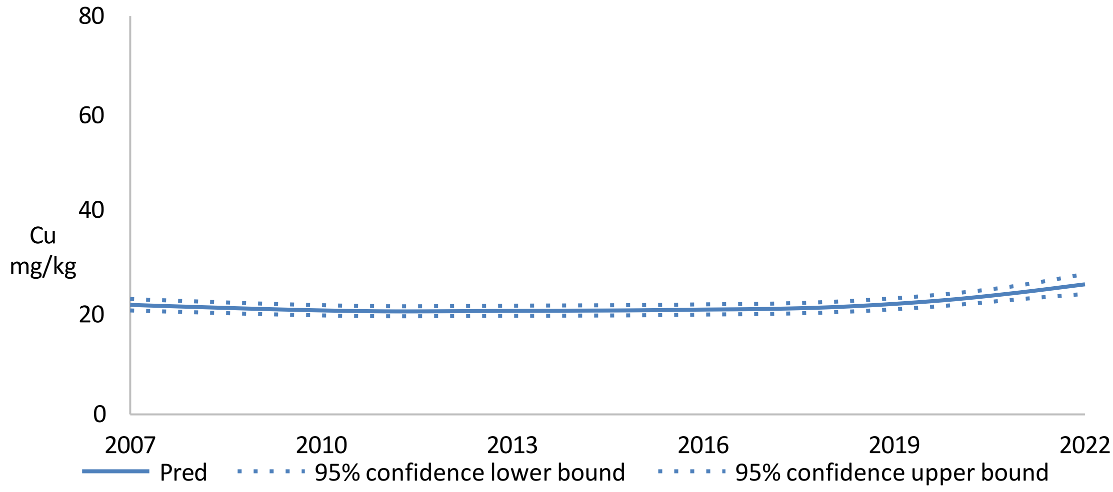

Figure 27. Change in mixed modelling average Cu concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

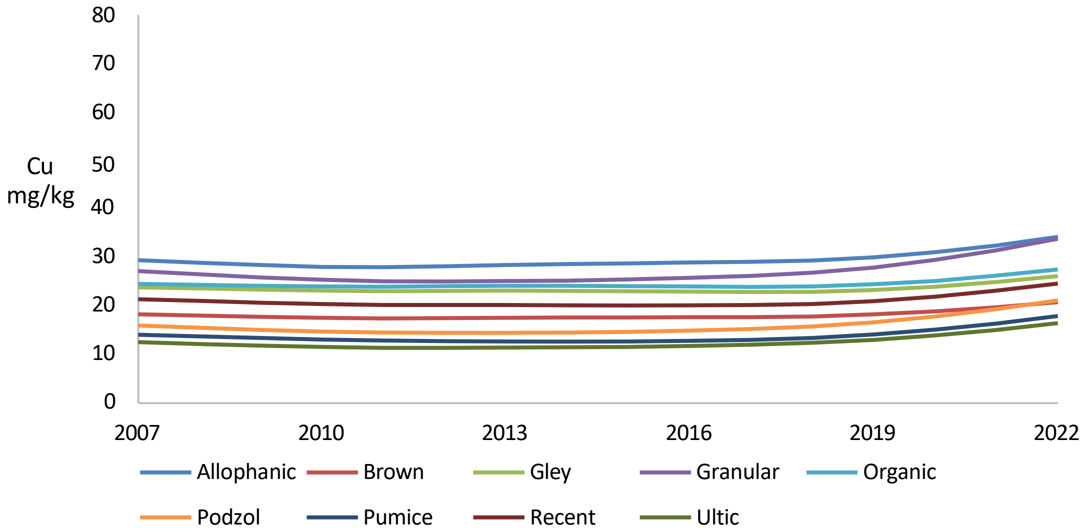

Figure 28. Change in mixed modelling average Cu 2007-2022 by soil order

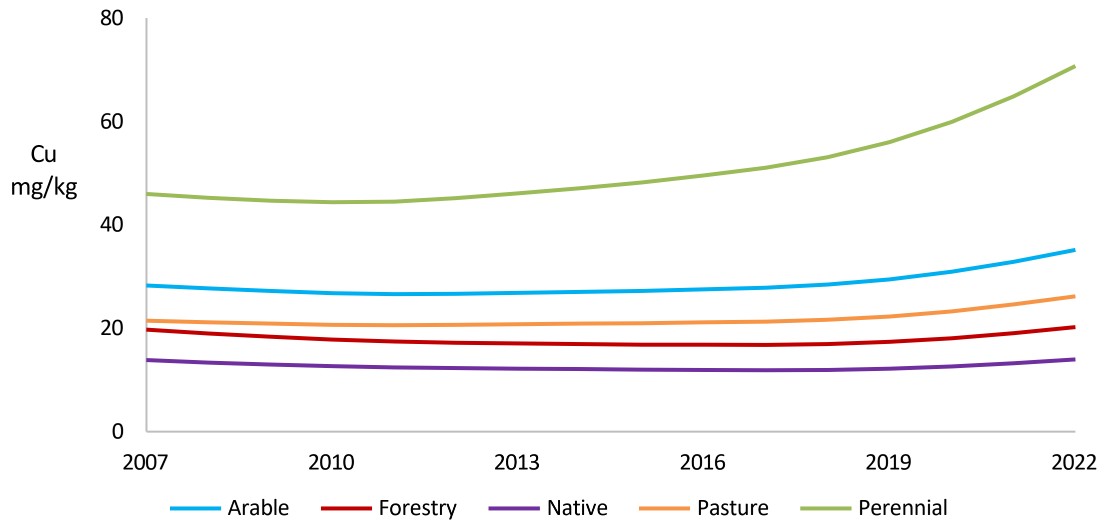

Figure 29. Change in mixed modelling average Cu 2007-2022 by land use.

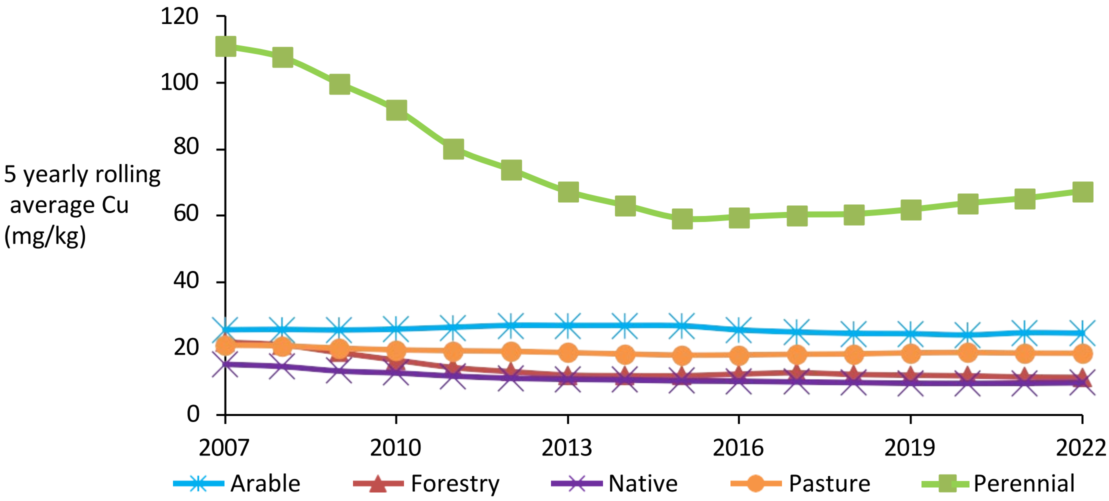

Figure 30. Average Cu by land use 2007-2022. The soil guideline value for typical agricultural soils for the protection of ecological receptors for Cu is 130 mg/kg (Cavanagh 2019). The concentration below which deficiency could potentially occur is 5 (Alloway 2008a).

Fluorine (F)

Even though F is now thought of as an essential element in animals (Salminen et al. 2005), including humans, excessive levels result in fluorosis, and F is considered one of the most significant groundwater contaminants in some countries (Jha et al. 2011a). Addition of F impurities in phosphate fertilisers is considered a major source of anthropogenic contamination in New Zealand soils (Kim et al. 2016), so is of particular concern to the Waikato Regional Council. Previous work at Waikato Regional Council, ranking diffuse contamination issues according to their real or potential impacts, ranked accumulation of fluoride in rural soils through use of phosphate fertilisers as the 2nd most important issue in the soils domain and the 4th most important across all environmental domains (Unpublished technical report TR21-04 Inventory and prioritisation of diffuse contamination issues in the Waikato Region – update 2018; Discover document number 13341581, Kim et al. 2020). A natural source of F in New Zealand is volcanic eruptions (Cronin et al. 2000).

Although there may be potential human health effects, the main health impact of excessive F in New Zealand is seen in animal welfare. Additional environmental effects from F accumulation in soils include toxicity, alterations to soil chemistry and function, and wider cross-compartment contamination. Toxicity concerns include those to soil organisms and terrestrial wildlife (Pascoe et al. 2014), phytotoxicity (Arnesen, 1997; Manoharan et al. 2007; Stevens et al. 1997), chronic fluorosis in grazing animals (Loganathan et al. 2001; Loganathan et al. 2008; Stacey et al. 2010), and potential for aluminofluoride complexes to interfere with biochemical signalling pathways. AlFx complexes are of toxicological interest because they act as phosphate analogues in a variety of enzymes (Strunecka et al. 2012; Façanha & Okorokova- Façanha 2002). Alterations of soil chemistry and function include reduced turnover of SOM (Rao and Pal, 1978) and phosphatase activity (Poulsen, 2011), accelerated aluminosilicate weathering (Egli et al. 2001; Taylor et al. 2012), induced formation of AlFx complexes in pore-water (Manoharan et al. 1996), and altered uptake of F, Al, AlFx and other F-complexed elements in crops and animals (Barbier et al. 2010; Stevens et al. 1997). Wider environmental impacts include potential for contamination of groundwater (Loganathan et al. 2006), toxicity to aquatic ecosystems (Camargo 2003), and perturbation of the atmospheric F cycle from fluorinated gases released from fertilised soils or during fertiliser manufacture (Mizane and Lassis, 2012). In addition, volatile F-containing species are effective greenhouse gases (Brown et al. 2014).

The accumulation of F in soil is likely to increase uptake of F in all stock, not just those exposed directly to phosphate fertiliser, as plant uptake of F increases, and as ingestion of soil is the major source of dietary F (93% of dietary F, Grace et al. 2005). Recently, Wehrle-Martinez et al. (2024) reported sub-clinical fluoride toxicosis may be linked to spontaneous humeral fractures in first-lactation dairy cows in New Zealand. Cronin et al. (2000) estimated that for sheep, the tolerance limit for dietary F should be reached at soil F concentrations ranging from 370 to 1460 mg/kg, while for cattle the range was 330 to 1090 mg/kg. Cavanagh (2019) developed provisional added contaminant limits for F (130 mg/kg for agricultural land), however, given the uncertainty of the estimates, they are not recommended for use. In comparison, F concentrations found in this study ranged from 70-900 mg/kg.

Death of free-range stock grazing pasture after fertiliser addition is reasonably common (e.g. 3-4 animals per year in the Waikato, Pers. Com. Ross Vowles, Glenview Vets), and euphemistically called phosphate poisoning (O'Hara et al. 1982). During the period 1965-75, a total of 37 poisoning outbreaks were reported in NZ by the Ruakura Animal Health Laboratory. Frequently, F-containing fertiliser had been applied to pasture carrying frost or dew that dried on the foliage in the absence of rain (Edmeades 2004). Normally, rain washes the F-containing fertiliser of the foliage and into the soil, but here, the full load of F remained on the pasture.

However, the potential risk of chronic fluorosis occurring in animals grazing pastures in NZ is usually low if there is sufficient pasture cover and fertiliser is washed into the soil (Grace et al. 2008). A reason for this is the proportion of F that is soluble is much lower in NZ agricultural soils than the proportion reported in the literature as these overseas sites had been contaminated with F from industry (Loganathan et al. 2006). However, the increase in periods and length of drought caused by climate change and excessive grazing of pasture from increased intensification are likely to increase bare land. Bare land results in greater soil uptake by grazing animals (eating plant roots when no above ground foliage is available) so are likely to inflate this risk. Lactating cattle are particularly sensitive to F due to their negative calcium balance (Loganathan et al. 2006).

Higher soil F concentrations in soil increase the risk of toxicity to terrestrial wildlife species (Ranjan and Ranjan 2015). Despite the occurrence of animal health issues and the high ranking of F in the priority listing in an unpublished technical report TR21-04 and in Kim et al. (2020), there is little guideline for total F in soil. No guideline values were found for F for agricultural land and the only guideline values for the protection of human health found were the Regional Screening Levels for Chemical Contaminants at Superfund Sites (US EPA regions 3, 6 and 9) accessed at http://www.epa.gov/region06/6pd/rcra_c/pd-n/screen.htm. These are 3100 and 41000 mg/kg for residential and industrial land respectively. Pascoe et al. (2014) derived Risk Based Concentrations for F in soil for an area contaminated by phosphate ore processing facilities in south-eastern Idaho for four wildlife species. Lowest Observed Adverse Effects Levels ranged from 659 mg/kg (deer mouse) to 2537 mg/kg (red-tailed hawk). However, in attempting to set soil guideline values for the protection of ecological receptors for F, Cavanagh (2019) was unable to develop a reliable guideline due to insufficient data and further study on the ecotoxicity of F is needed.

The mixed modelling results showed no significant trend overall ($p>0.05$, Figure 31). There were no significant ($p>0.05$) changes in trend or pattern for F by soil order (Figure 32) or land use (Figure 33), although there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). The volcanic soil orders, Allophanic, Granular and Pumice soils, had higher average total F concentrations, while Podzol, Organic and Ultic soils had lower average total F concentrations. As a natural source of F in New Zealand is volcanic eruptions (Cronin et al. 2000), some F in Allophanic, Granular and Pumice soils may be volcanic in origin.

As expected, fertilised land uses, arable, perennial and pasture, had higher total F concentrations than land in native land use, consistent with accumulation of F contaminants of phosphate fertiliser (Figure 34).

Monitoring of F should continue due to the potential risks to animals, humans and the environment. Further research into the ecotoxicity of F to inform soil guideline values should be encouraged.

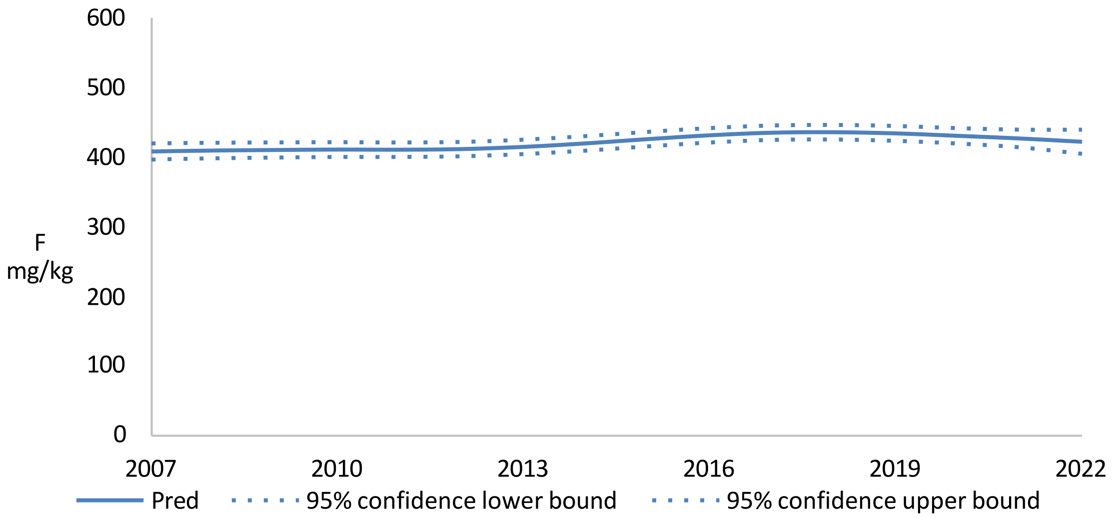

Figure 31. Change in mixed modelling average total F concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

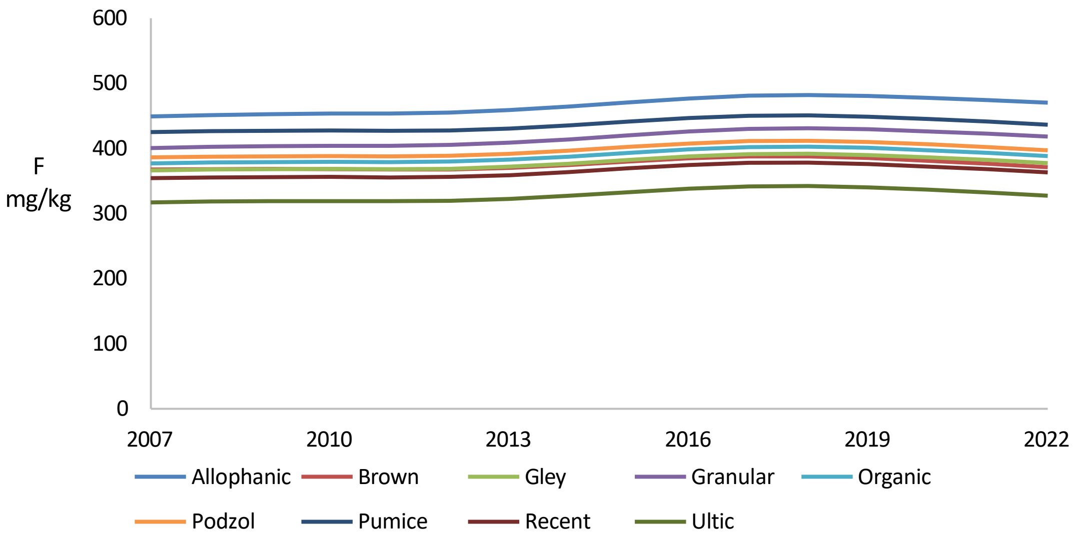

Figure 32. Change in mixed modelling average total F 2007-2022 by soil order

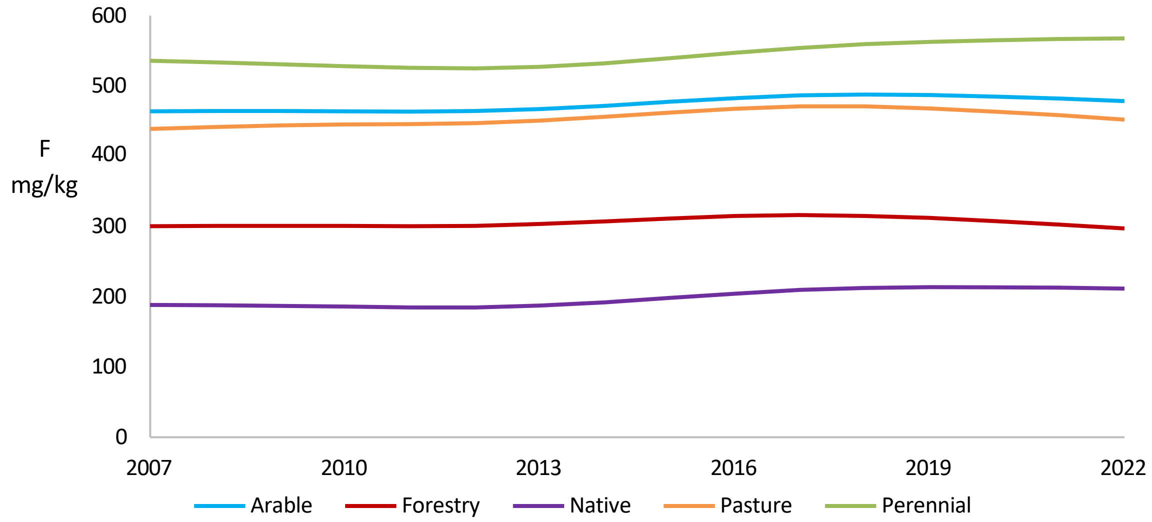

Figure 33. Change in mixed modelling average total F 2007-2022 by land use.

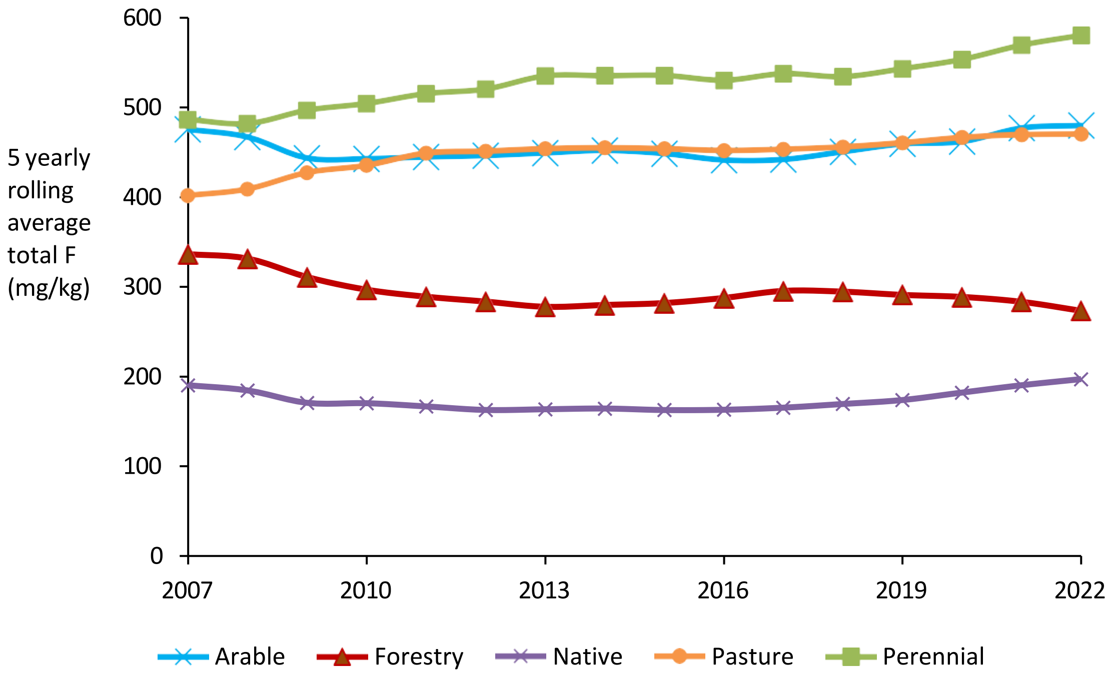

Figure 34. Average total F by land use 2007-2020. There is no soil guideline value for total F but effects on small mammals have been observed at F concentrations >650 mg/kg (Pascoe et al. 2014).

Lead (Pb)

Lead is described as having few competitors as a persistent harmful pollutant (Kabata-Pendias & Mukherjee 2007). It is a neurotoxin but also elicits responses in an extraordinarily wide range of biological and biochemical tests; among them tests for enzyme inhibition, fidelity of DNA synthesis, mutation, chromosome aberrations, cancer and birth defects. It reacts or complexes with many biomolecules and adversely affects the reproductive, nervous, gastrointestinal, immune, renal, cardiovascular, skeletal, muscular and hematopoietic systems as well as developmental processes (Johnson, 1998). Chronic exposures can permanently impair the brain's functioning, thus limiting a child's intellectual and social development (Mielke, 1999). Lead is a priority contaminant for resource managers in NZ and overseas (Kim & Taylor 2013, MfE 2011).

Natural sources of Pb in the Waikato region include weathering of geogenic materials, volcanic emissions, wind-blown dusts, sea spray, biogenic material, and forest fires (Hough 2010), while there are a multitude of past anthropogenic sources. The use of Pb has decreased significantly since the 1980's with the phasing out of Pb in roof flashing, petrol, paint, bullets, metal can solder, plumbing, pesticides and batteries (Tchounwou et al. 2012; Kabata-Pendias & Mukherjee 2007; Gaw 2006). However, Pb is still used in many products, such as brass or chrome tap fittings, aviation gas, electronics, fishing gear and tyre balance weights (Levin et al. 2021; Taylor & Kruger 2020).

In urban areas, the age of homesteads and other infrastructure with a legacy of Pb fittings drives Pb concentration in soil. Soil Pb concentrations were higher in homes with painted exteriors and generally increased with age of the home (Laidlaw et al. 2018). Soil dust containing legacy Pb has been reported to be a major source of Pb to households and a primary pathway of Pb exposure for children (Martin et al. 2023; Laidlaw et al. 2014).

The New Zealand Soil Contaminant Standard using the rural residential scenario for Pb is 160 mg/kg (MfE, 2011), while the Guideline value for the Protection of Ecological Receptors for non-food production and agricultural land uses (Cavanagh 2019) is 530 mg/kg. In comparison, the Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health for Pb in agricultural soil (CCME 1999) is 70 mg/kg, which is much more conservative. The Canadian guideline values are derived using a Total Dietary Input for the most sensitive receptor designated whereas the Guideline values for the Protection of Ecological Receptors for non-food production and agricultural land uses were derived using the lower of the value protective of 95% of crop and grass species or 80% of soil invertebrates (Cavanagh 2019).

An interesting issue that arose during monitoring were outliers in soils from past, often unrecorded, rifle ranges. Both Pb (lead in bullets) and Sb (in cartridge primer) concentrations were 100-fold higher than usual at these sites and are outliers, exceeding the soil guideline value for Pb for agricultural soils for the protection of ecological receptors (540 mg/kg). This data proved useful for identifying and locating lost or unknown rifle ranges. Single sites under cropping, forestry, perennial and native land use have been identified and these outliers were excluded from analysis.

The mixed modelling results showed no significant trend overall ($p>0.05$), (Figure 35). There were no significant ($p>0.05$) changes in trend or pattern for Pb by soil order (Figure 36) or land use (Figure 37). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Average Pb by Soil Order showed Granular soils had higher average Pb concentrations, while Podzols, Pumice and Organic soils had the lower average Pb concentrations.

Mixed modelling calculated results showed average Pb for the perennial land use was noticeably higher than other land uses although this differed from the 5-year rolling average results where perennial was similar to other land uses and arable average Pb was higher (Figures 37-38). Results measured tended to vary over 5 mg/kg, suggesting sampling or analytical errors, while all land uses have concentrations similar to native land use. There are multiple sources of legacy Pb in the Waikato region (Pb-petrol, Pb-Sb-tyre weights, Pb-containing paint, Pb-containing pesticides and remobilised dust from these sources), which do not decay but remain in soil.

Except for the suspected historic rifle range sites, all sites met the guideline value for agricultural soils for the protection of ecological receptors. However, monitoring should continue due to the potential toxicity of Pb to humans and the environment.

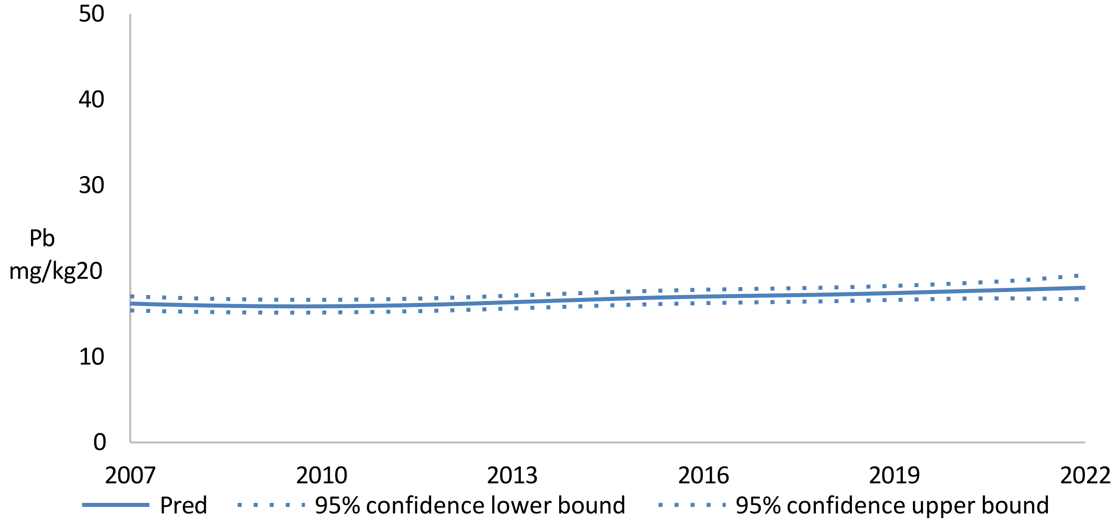

Figure 35. Change in mixed modelling average Pb concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

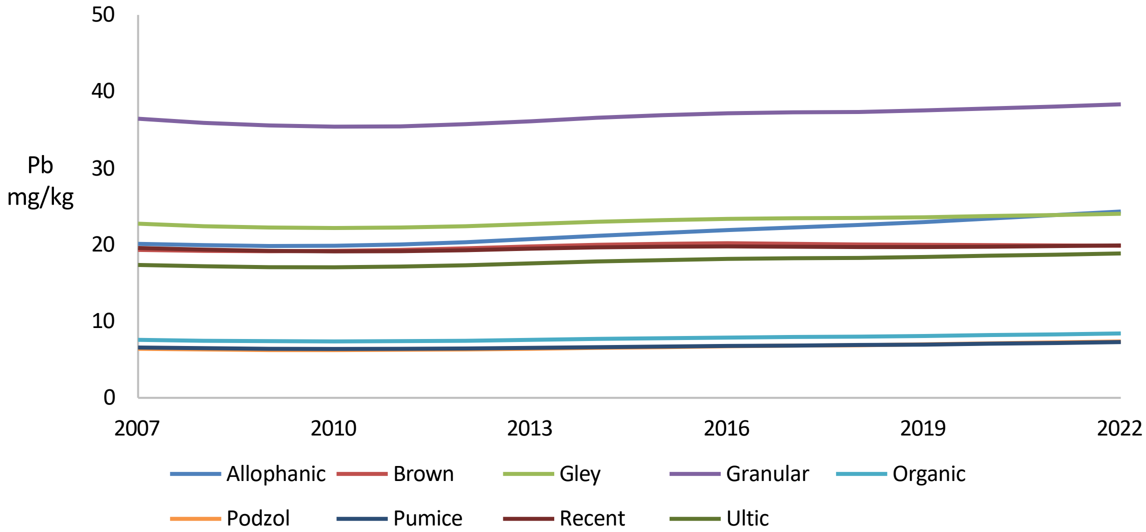

Figure 36. Change in mixed modelling average Pb 2007-2022 by soil order

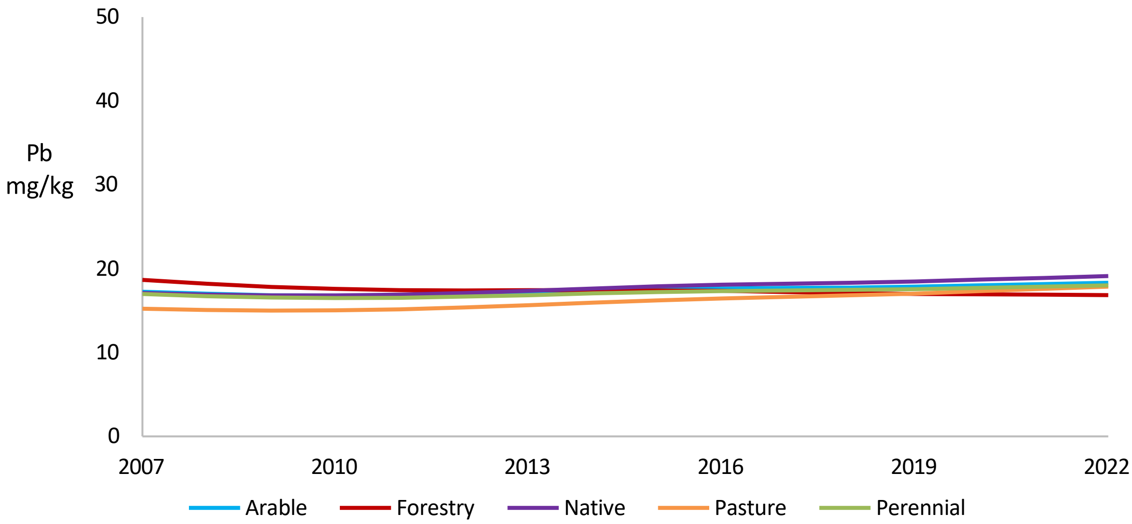

Figure 37. Change in mixed modelling average Pb 2007-2022 by land use.

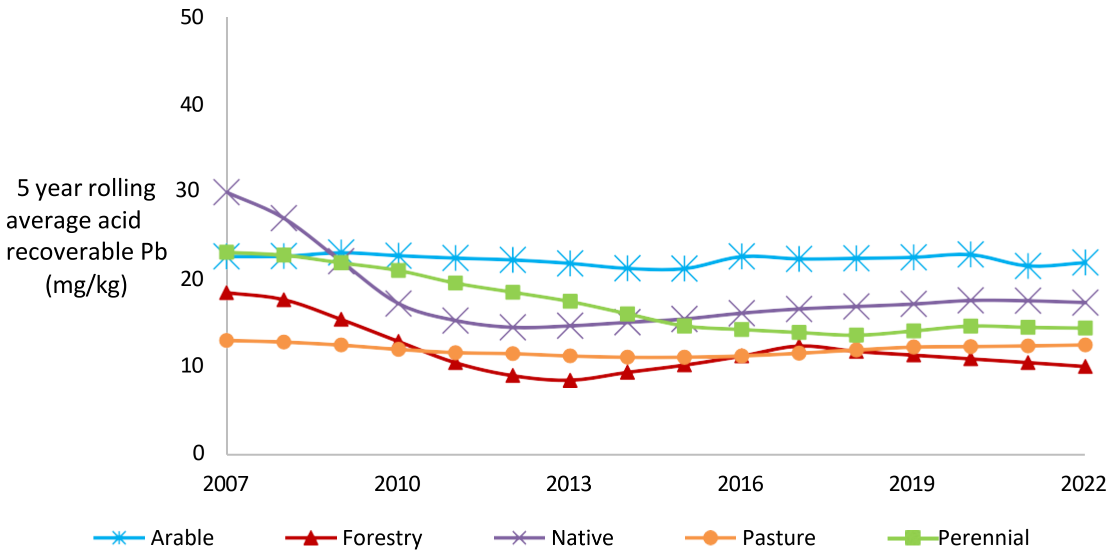

Figure 38. Average Pb by land use 2007-2022. The soil guideline value for agricultural soils for the protection of ecological receptors for Pb is 530 mg/kg.

Nickel (Ni)

Nickel is an essential nutrient for animals and a beneficial element for plants, but elevated Ni concentrations in soils can have potential negative impacts on plants, microorganisms and animals (Ma and Hooda 2010). Nickel sorption and mobilisation in soil is complex, being influenced by soil pH, redox, and the chemistry of Fe, Mn, Mg, and DOC (Rinklebe & Saheen 2017; Uren 1992).

The major sources of Ni to agricultural soils in the Waikato region are likely to be atmospheric deposition and mineral phosphate fertilisers, although application of livestock manures is also a major source of Ni for many other countries (Ma & Hooda 2010). In the absence of mining or smelting of Ni, anthropogenic Ni is released to the atmosphere from the burning of fossil fuel. So, the average annual atmospheric deposition flux of Ni is quite low, about 0.95 mg/m^2/y (Ma & Hooda 2010). However, there is considerable fertiliser use in the region. Taylor (2016) reported Ni in phosphate rock used in New Zealand fertilisers ranged from 1-105 mg/kg, while the median of Ni in 40 superphosphate samples from around the world was 25 mg/kg.

No New Zealand risk-based guideline value was found for Ni and two overseas risk-based guideline values for agricultural soils were used, the USA Ecological Soil Screening Level protective of ecological receptors (EPA, 2005, revised 2007) of 38 mg/kg and the Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health in agricultural soils of 50 mg/kg.

The mixed modelling results showed there was a significant increasing nonlinear trend overall (p=0.019, Figure 39) but there were no significant (p>0.05) changes in trend or pattern for Ni by soil order land use (Figure 40). However, there were significant differences between land uses (p<0.01) and soil orders (P<0.01). Granular, Recent and Gley soils had higher average Ni concentrations than other soil orders, while Podzols, Pumice and Ultic soils had the lowest average concentrations (Figure 41). Granular soils have high concentrations of iron minerals that have high affiliation to adsorb Ni (Ma and Hooda 2010). Taylor (2016), while investigating the fate of trace elements found in fertilisers, used PCA to show Ni in New Zealand soils was associated with Fe, Cr and V. Similar strong correlation between natural Cr and Ni was also reported in Salminen et al. (2005). As most Cr in Granular soils is expected to be natural (Section Chromium above) it seems likely that a large proportion of the Ni in Granular soils is natural.

Perennial and arable land uses had higher average Ni concentrations, while pasture was also elevated, compared to native and forestry land uses (Figures 41-42). The application of Ni impurities in phosphate fertilisers is the likely source of Ni elevation.

No samples exceeded the Ecological Soil Screening Level protective of ecological receptors (EPA, 2005, revised 2007) or the Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health in agricultural soils. Currently, there are no apparent issues with Ni in the Waikato region.

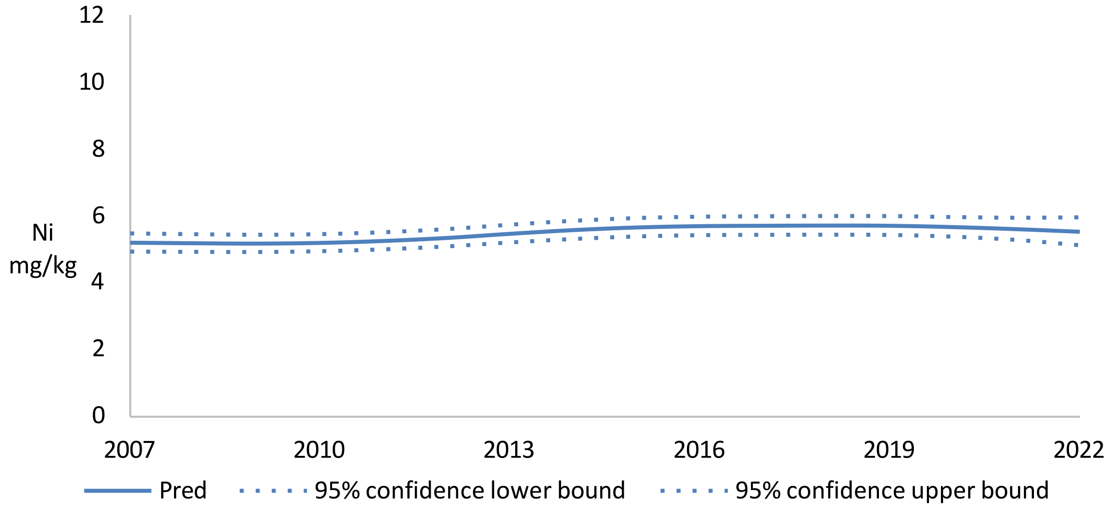

Figure 39. Change in mixed modelling average Ni concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

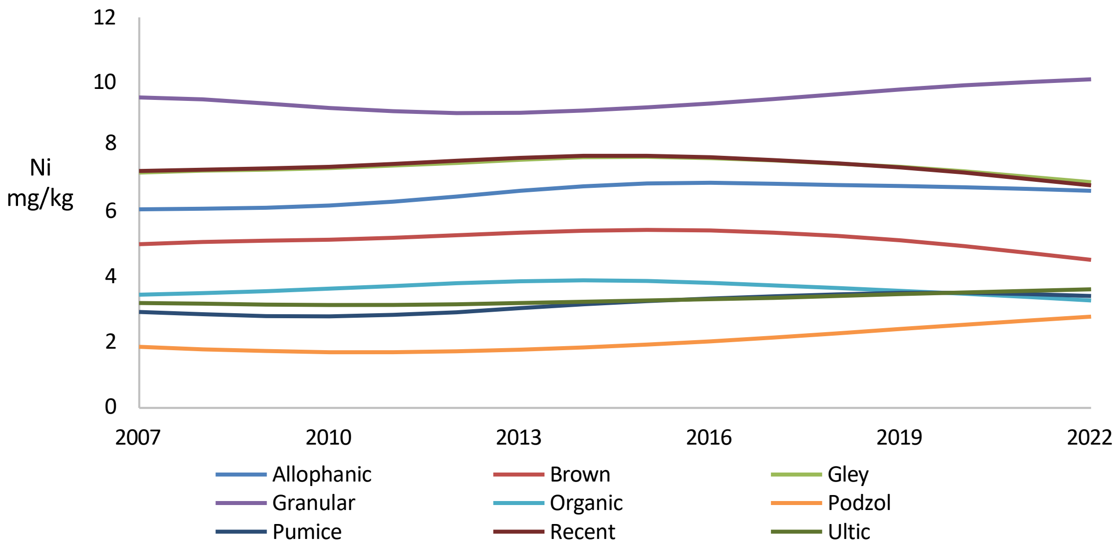

Figure 40. Change in mixed modelling average Ni 2007-2022 by soil order

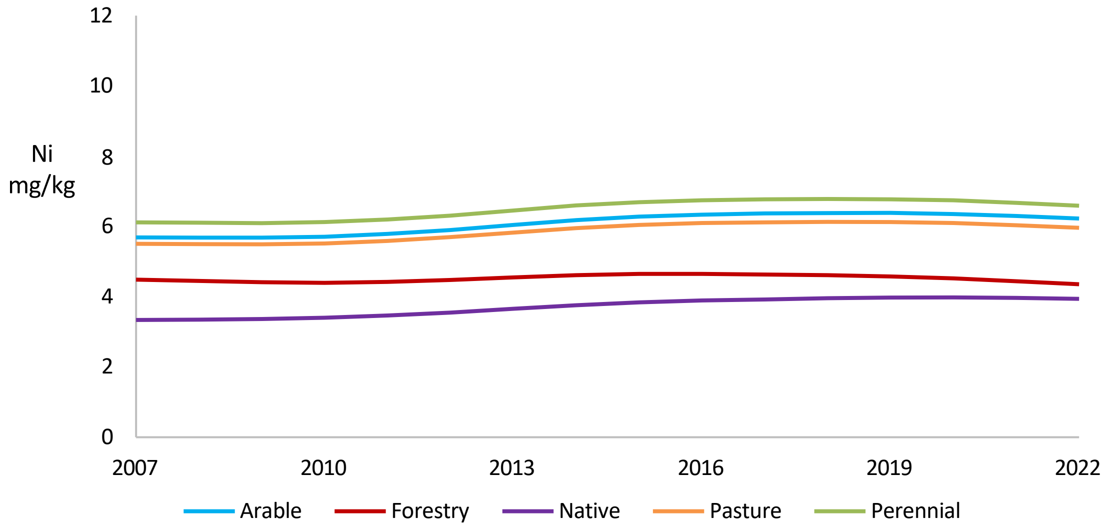

Figure 41. Change in mixed modelling average Ni 2007-2022 by land use.

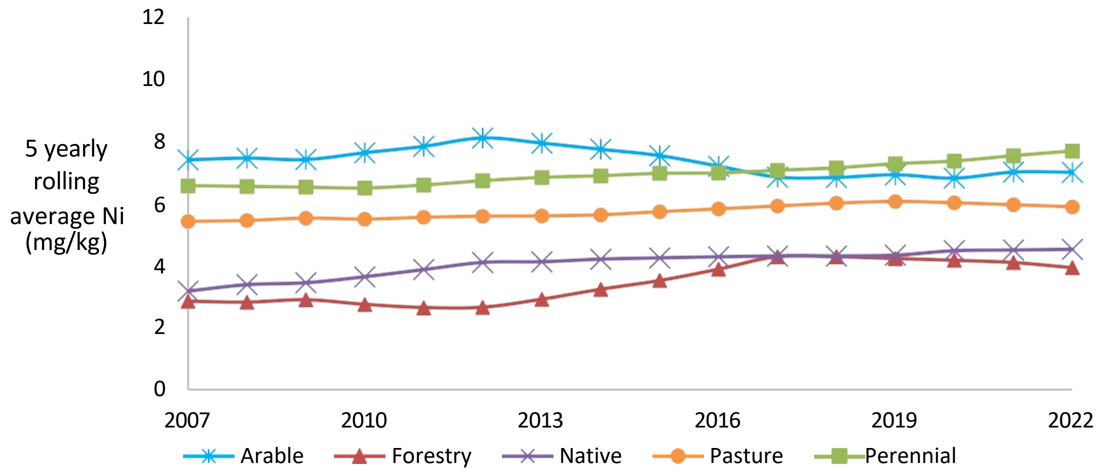

Figure 42. Average Ni by land use 2007-2022. The Ecological Soil Screening Level for Nickel which is 38 mg/kg: (EPA, 2005, revised 2007).

Zinc (Zn)

Zinc is essential to plants and animals, and it ranks as the third most important limiting nutrient element, next to N and P, in crop production (Gowariker et al. 2009). Hidden Zn deficiency has become increasingly common in many areas and is generally associated with growing Zn-inefficient varieties on soils of marginally low available Zn status (Alloway 2009; 2008a,b). Hidden Zn deficiency may be an issue for gleyed or sandy soils in the Waikato region due to their naturally low Zn contents, but normal farming practices for dairy, sheep and beef, make deficiency extremely unlikely for animals. Alloway (2008a) suggested concentrations <10 mg/kg could indicate deficiency.

However, excessive Zn concentrations have high toxicity to microorganisms and some plants, impacting a wide range of biological processes, so Zn is considered a priority contaminant by NZ resource managers (MfE 2011). Also, soil microorganisms and invertebrates tend to be more susceptible to Zn toxicity than higher plants or aquatic organisms because they have less well-developed homeostatic mechanisms. Results of inhibition of microorganisms and invertebrates include accumulation of litter due to reduced decomposition, and the failure of Rhizobium species in nodules on the roots of legumes to fix atmospheric nitrogen. A sign of Rhizobium species failure in the field are signs of nitrogen deficiency in legume plants (Alloway 2008b). Nitrogen fixing Rhizobia bacteria are relatively susceptible to Zn toxicity and so this economically important group is notably vulnerable to excessive accumulation of Zn in soil. Reduction in these species would necessitate the increased use of N fertilisers to compensate for the lack of fixed nitrogen with ongoing economic and environmental consequences. Nematodes and enchytraeids are also sensitive to Zn concentrations (Creamer et al. 2008). Zn is also considered strongly bioaccumulative by earthworms (Richardson et al. 2015).

There are multiple major sources of Zn contamination to the environment in the Waikato region. Sources include mineral and organic fertilisers, 369 veterinary medicines, 35 registered pesticides, galvanised (Zn coated) iron, Zn paint, tyre rubber and human sewage discharges. One other major source in NZ is likely to be the treatments and preventatives of the fungal disease facial eczema (Figure 43). Preventive treatment includes dosing animals to subtoxic levels with Zn, either in drinking water, as boluses or directly injected. Facial eczema associated Zn was estimated to contribute about 8500 t of Zn per year to the environment in the Waikato region (Kim 2005). Wide use of Zn treatments continues across the Waikato region, and these are advertised by all major agricultural rural supply businesses.

As there is no New Zealand risk-based guideline protective of human health for Zn, the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health for copper and Zn in agricultural soil (CCME 1999) was identified as the nearest international risk-based match for local environmental conditions and used for comparison. The CCME guideline value for Cu is 63 mg/kg and for Zn it is 200 mg/kg, while the Guideline value for the Protection of Ecological Receptors for non-food production and agricultural land uses for typical soil and aged Zn (Cavanagh 2019) is 190 mg/kg.

The mixed modelling results showed no significant trend overall ($p>0.05$), (Figure 44). There were no significant ($p>0.05$) changes in trend or pattern for Pb by soil order (Figure 45) or land use (Figure 46). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Allophanic, Granular, Gley, Brown and Recent Soils had higher Zn concentrations, while Pumice, Organic, Podzols and Ultic soils had lower Zn concentrations. There results were expected as there are quite complex interactions between Zn and soil. Clay minerals and SOM can bind Zn strongly, especially at neutral and alkaline pH, and control solubility and bioavailability. While Zn is usually moved down a soil profile due to leaching, plant uptake and subsequent decay readily transports Zn from sub-surface minerals soil to the soil surface (Steinnes & Friedland 2006). SOM can also bind Zn but organo-Zn complexes may still be relatively mobile (Kabata-Pendias & Murkherjee 2007), e.g. Zn in soil solution in a slightly acid loamy fine-sand was attributed to manure from grazed cattle (Anguelov & Anguelova 2009) probably as organo-Zn complexes of Dissolved Organic Matter (DOM). So, soil is acting both as a sink and a source for Zn.

Both mixed modelling and measured values showed sites under perennial had higher average Zn concentrations than other land uses (Figures 46-47) and were consistently near the NZ soil guideline value for the protection of ecological receptors (Cavanagh 2019). Arable sites also had elevated average Zn compared with native sites, probably from similar sources to horticultural sites. Pasture sites had similar concentrations to arable, but these are likely from different sources, the treatment for facial eczema and other animal remedies (Kim & Taylor 2017). Thirteen samples (about 2% of samples) from pasture, perennial and arable land uses exceeded the soil guideline value of 130 mg/kg. These results suggest considerable use of Zn, perhaps in pesticides or in applications of trace element fortified fertilisers in horticultural management.

In comparison, sites under forestry and native had the lowest average Zn concentrations and one forestry site had Zn concentrations below the level where deficiency could occur.

Monitoring of Zn should continue due to the number of sources of Zn and the current levels in soils. Advice should be provided to landholders where the soil guideline value for typical agricultural soils for the protection of ecological receptors for Zn of 130 mg/kg is exceeded.

Figure 43 Examples of the fungal disease facial eczema. Dosing animals with Zn prevents this decease (Waikato Regional Council).

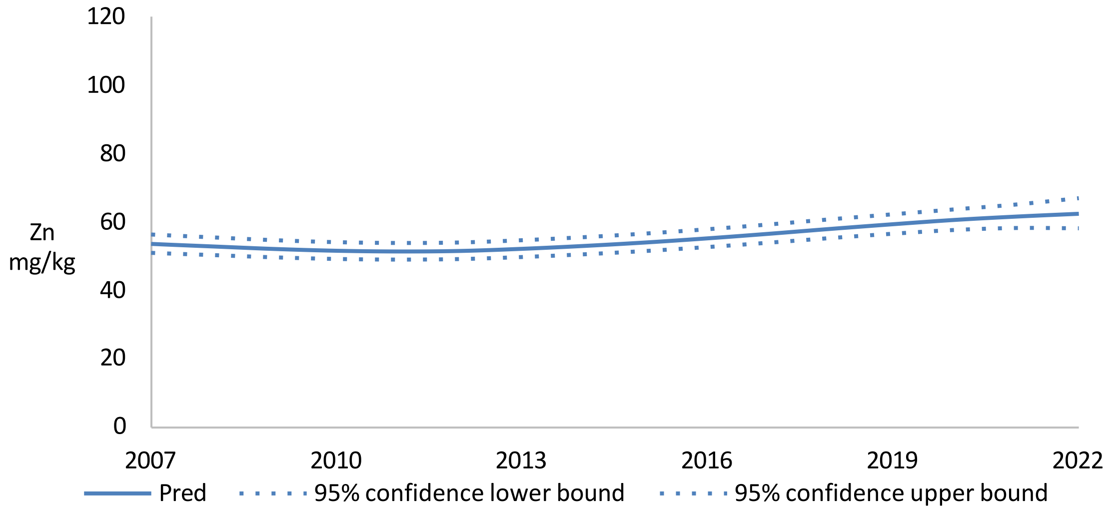

Figure 44. Change in mixed modelling average Zn concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

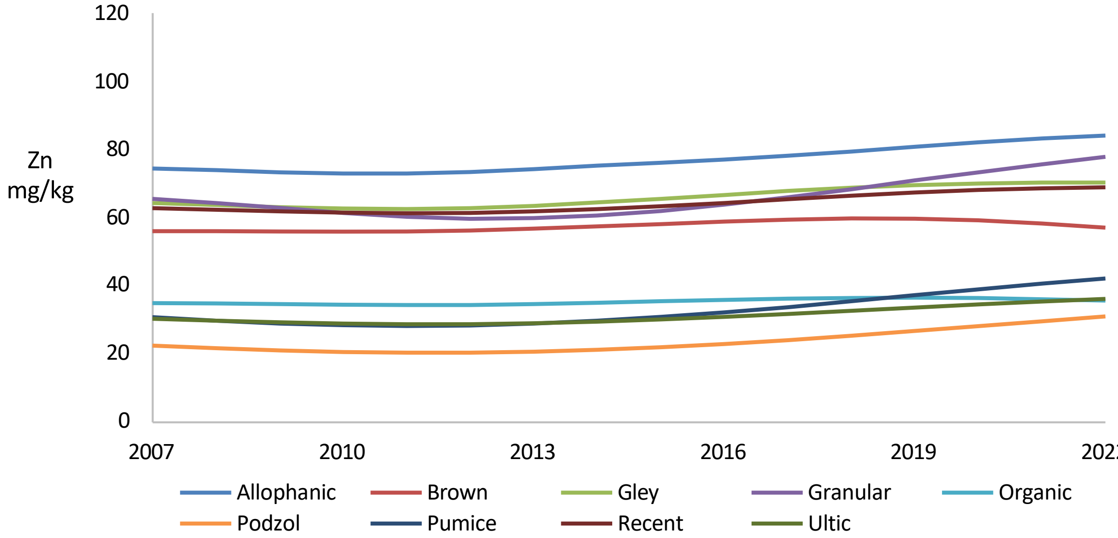

Figure 45. Change in mixed modelling average Zn 2007-2022 by soil order

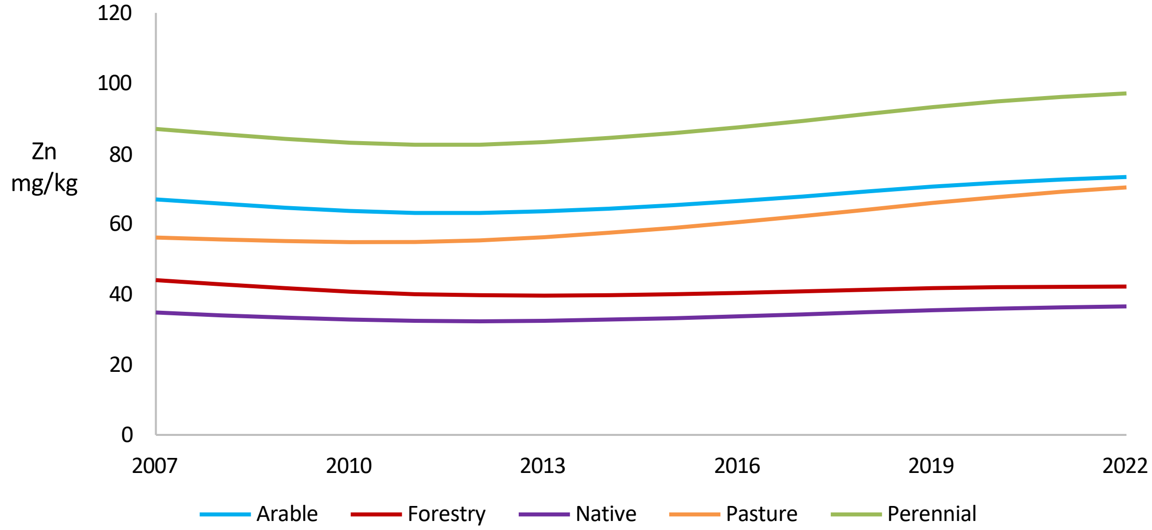

Figure 46. Change in mixed modelling average Zn 2007-2022 by land use.

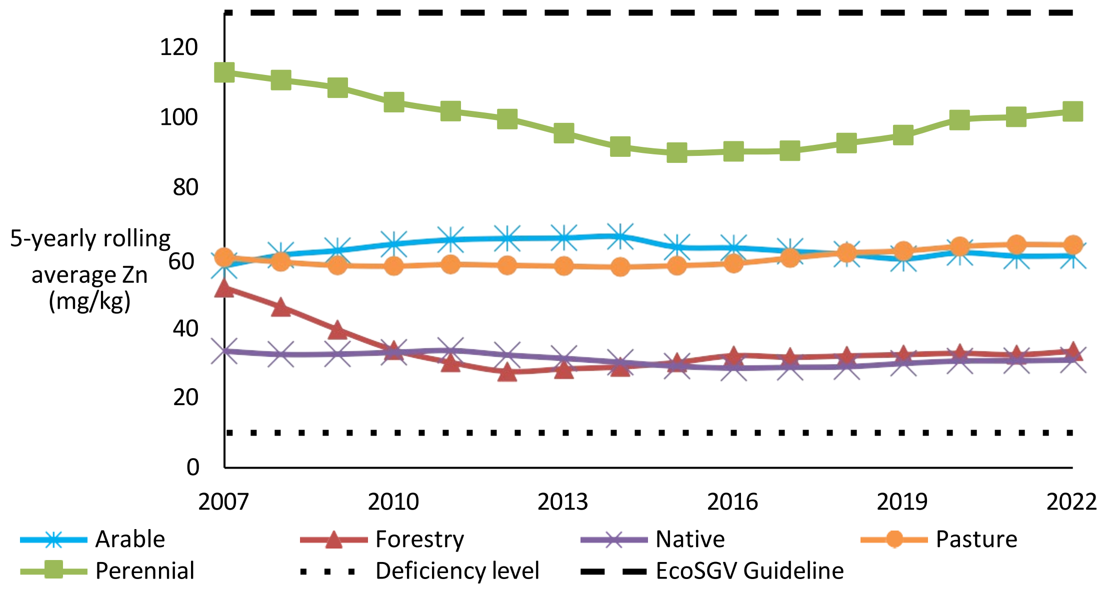

Figure 47. Average Zn by land use 2007-2022. The upper guideline is the NZ soil guideline value for the protection of ecological receptors in typical soils in agriculture (Cavanagh 2019). The lower guideline is the level at which deficiency could occur (Alloway 2008a).

Boron (B)

Boron is a micronutrient critical to the health of most plants. Plants get most of their B from decomposing organic matter in the soil. Boron is highly mobile in soil and easily washed out in drainage which can lead to boron deficiency in New Zealand (Skinner et al. 2003). However, Boron has one of the smallest ranges between deficiency and toxicity of all the trace elements, but there is great variation in the requirement and tolerance of B by different plant species (Paull et al. 1988).

Major natural sources of B in the Waikato are rock weathering, sea water aerosols and from geothermal activity, while anthropogenic sources are fertilisers, animal supplements, timber preservatives and commercial materials. Median-high B concentrations were found in all fertilisers derived from P rock (130-500 mg/kg, Taylor 2016). Boric acid is commonly used as a timber preservative throughout the Waikato region and New Zealand (Robinson et al. 2007), so B may leach into the soil from timber framing. Boron is also widely used to produce commercial materials such as insulation, glass fibres, bleaches, borosilicate glass, herbicides and insecticides (Schnurbusch et al. 2010) and as powder coatings to prevent corrosion and oxidation (Petrova et al. 2007). Although the size of these industries in New Zealand is small compared to Europe, when combined with imports, these items do appear to be a minor source of B to the environment.

There are very few guideline values internationally and no suitable New Zealand guideline value for B as measured in soil quality monitoring. The is no limit for B under the Methodology for Deriving Soil Guideline Values Protective of Human Health (MfE, 2011), while the guideline value for the protection ecological receptors (Cavanagh 2019) requires the hot water extractable B method. However, the extraction method in soil monitoring is acid recoverable B, not hot water extractable B, which are commonly used to assess plant toxicity. The risk-based guideline that was the nearest approximation for agricultural land was the Health Investigation Level for residential land with garden from the Australian Guideline on the Investigation Levels for Soil and Groundwater (NEPC 1999). This guideline value is 3000 mg/kg and all sites were well below this level.

The mixed modelling results showed no significant ($p>0.05$) change in B for the overall data (Figure 48) and there were no significant ($p>0.05$) changes in trend or pattern for B by soil order

(Figure 49) or land use (Figure 50). Nevertheless, there were significant differences between land uses (p<0.01) and soil orders (P<0.01). Allophanic soils had the highest average B concentrations while Podzols, Pumice and Ultic soils consistently had the lowest concentrations. Allophanic soils have strong anion exchange capacity to bind anions like B. Both mixed modelling and 5-yeary rolling averages showed horticultural soils had higher average B concentrations than other land uses and considerably higher than land in native vegetation (Figures 50-51). Further investigation revelled soils in kiwifruit production had significant accumulation. This is surprising as kiwifruit is a B sensitive crop. Excessive B reduces fruit yield and is associated with premature ripening in cool storage (Smith et al. 1985). Kiwifruit is a high intensity crop, thus the high B concentrations could be explained by high P fertiliser inputs. However, B in irrigation water or leaching from treated timber framing used to grow the vines may add to total B inputs. Both river and ground waters may be used for irrigation of kiwifruit.

Taylor (2016) reported a large amount of the B applied in fertilisers was not accounted for. This result was explained by B mobility, as it can easily be transferred to surface water. Thus, some lakes and streams measured in Taylor (2016) periodically exceed the B trigger value for freshwater protection for 95% of aquatic species (0.37 g/m, ANZECC 2000). Interestingly, rainbow trout, an important game fish in the Waikato region, was the most sensitive fish species reported by WHO (1998) with NOECs ranging from 0.009-0.103 g/m.

Taylor (2016) also reported accumulation of B in estuarine sediments, consistent with the established view that B is incorporated into fine-grained sediments once it reaches the marine environment (Boon & MacIntyre 1968, Liss & Pointon 1973).

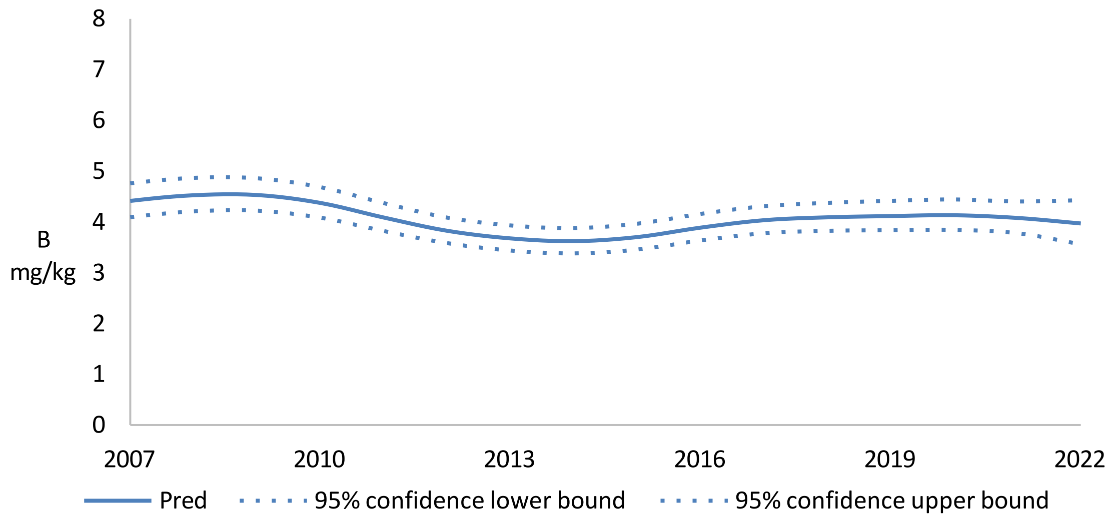

Figure 48. Change in mixed modelling average B concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

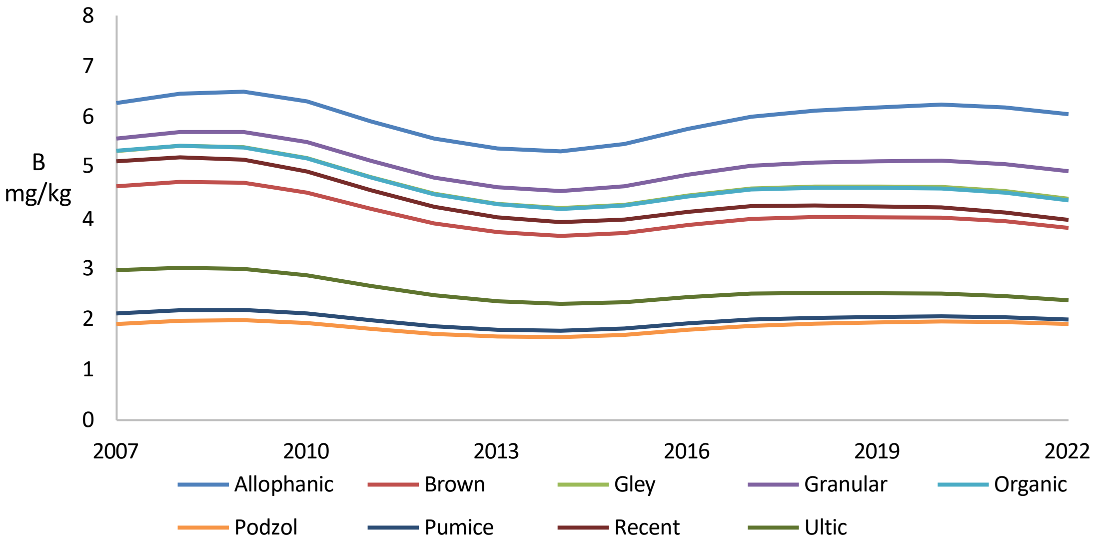

Figure 49. Change in mixed modelling average B 2007-2022 by soil order.

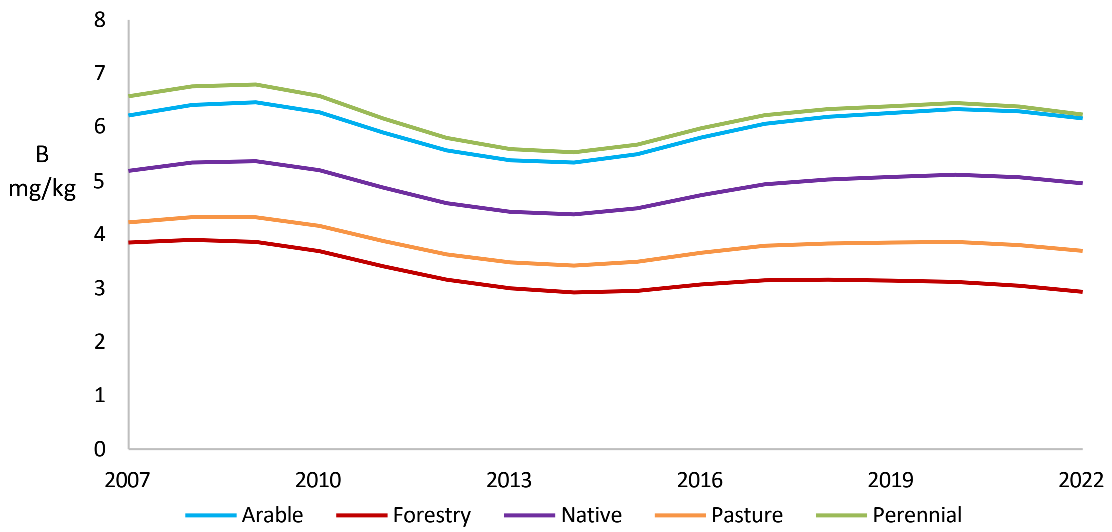

Figure 50. Change in mixed modelling average B 2007-2022 by land use.

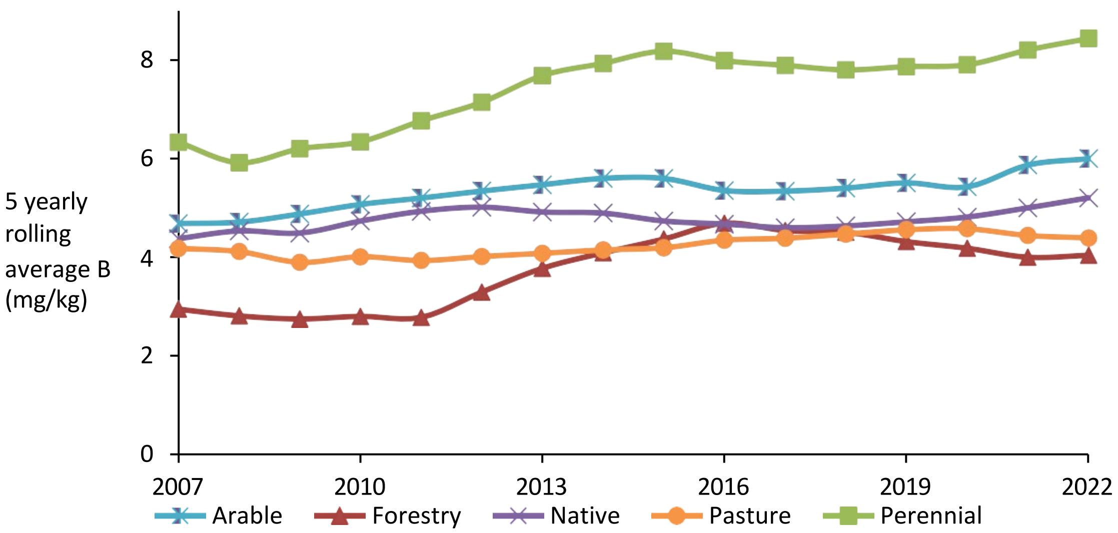

Figure 51. Average B by land use 2007-2022. Results are well below the Australian Health Investigation Level for residential land with garden of 3000 mg/kg (NEPC 1999).

Cobalt (Co)

Cobalt is essential for prokaryotes, including nitrogen fixing bacteria, mammals, including humans, many lower plants, such as marine algal species including diatoms, chrysophytes, and dinoflagellates. It may be essential, or at least beneficial, for higher plants in the family Fabaceae or Leguminosae (Hu et al. 2021). However, in the Waikato region, soils of the Central Volcanic Plateau and soils dominated by the Taupo and Kaharoa ashes have very low natural Co levels resulting in bush sickness, a wasting disease that made farm animals look as if they were starving despite having adequate food (Tonkin undated; Grange & Taylor 1932). Nowadays, Co-fortified superphosphate or direct Co supplements are used by animal farm operations to alleviate Co deficiency.

There was no suitable New Zealand guideline for Co and are very few guideline values internationally. No suitable guideline value for agricultural land was found so guideline values considered were for residential land. The Australian guideline for the protection of human health, Residential with garden/soil access and <10% produce consumption, no poultry, gives an Investigation Level for Co in Soil of 100 mg/kg and a Remedial Urgency level of 190 mg/kg (NEPC, 1999). This remedial urgency value is also protective of ecological health. Another guideline considered was the USA Ecological Soil Screening Levels (US EPA, 2005), which gives guideline values for Co for the protection of soil invertebrates (13 mg/kg), avian species (120 mg/kg) and mammals (230 mg/kg). Finally, the Regional Screening Levels for Chemical Contaminants at Superfund Sites (US EPA regions 3, 6 and 9) give a screening level for Co for residential land for human health of 23 mg/kg.

The lowest guideline value was the USA Ecological Soil Screening Level of 13 mg/kg for soil invertebrates and 7% of farmed and forestry sites exceeded this value, with a maximum value of 29 mg/kg. The highest values were found for land in the process of reverting to scrub, far from any known Co source, with minimal or nil historic fertiliser application, so likely only natural Co. This result suggests New Zealand-based guideline values are needed rather than attempting to use overseas guideline values. In addition, the ecological integrity of farmed landscapes is likely compromised by farming practices, like cultivation, application of fertilisers and agricultural chemicals, and effects of farming animals. So, a guideline protective of all ecological receptors is impractical for land in agriculture or forestry.

Hawke et al. (1994) presented concentrations below which bush sickness could occur as <2 mg/kg and about 25% of sites in the Waikato Region were below this value. Farm animals at these sites would likely require Co supplements. However, the availability of Co in soil is mainly driven by pH. Adsorption of Co^{2+} on soil colloids is high between pH 6 and 7, whereas leaching and plant uptake are enhanced at lower pH (USEPA 2005). Pastoral soils in the Waikato region have an average pH of about 5.8.

The mixed modelling results showed no significant trend overall ($p>0.005$), (Figure 52). There were no significant ($p>0.05$) changes in trend or pattern for Co by soil order (Figure 53) or land use (Figure 54). Nevertheless, there were significant differences between land uses ($p=0.005$) and soil orders ($P<0.001$). Granular and Recent soils had higher concentrations of Co, while Podzols, Pumice and Organic soils had lower concentrations (Figure 53). Fertilised land uses had slightly higher concentrations of Co compared with non-fertilised land uses (Figures 54-55). The most likely cause of Co elevation in New Zealand is application of fertilisers deliberately fortified with Co, Co impurities in fertilisers, or dung from animals fed Co-supplements.

Looking at the individual site data, Granular soils had the highest concentration, while Podzols, Pumice and Organic soils had Co concentrations below which bush sickness could occur. A single Allophanic site and some low fertility brown soils also had Co concentrations below which bush sickness could occur (<2 mg/kg, Hawke et al. 1994).

About three quarters of sites in the region have Co concentrations >2mg/kg, so stock are unlikely to suffer bush sickness on these sites. There is no evidence of accumulation of Co in soil in the Waikato region.

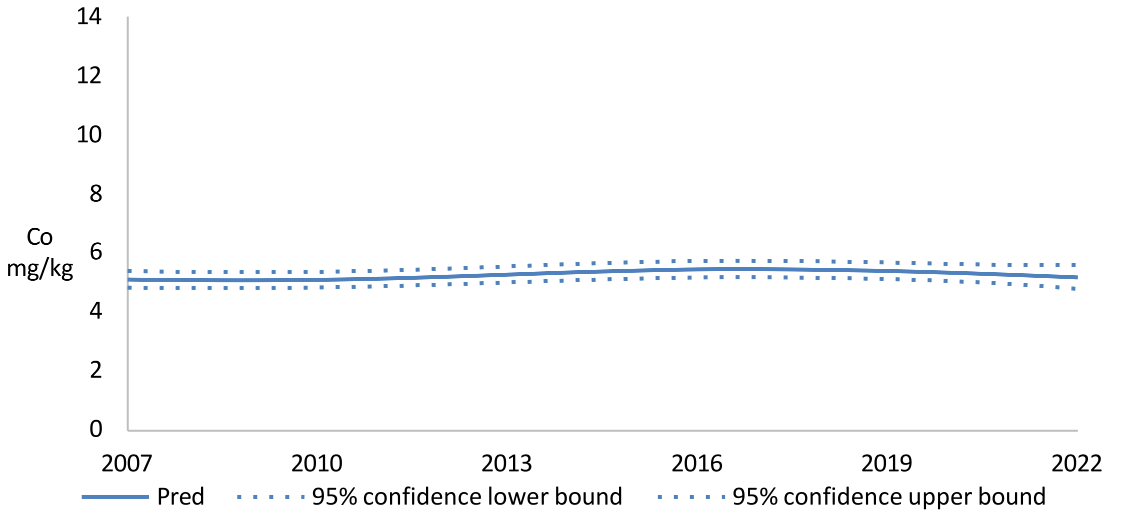

Figure 52. Change in mixed modelling average Co concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits

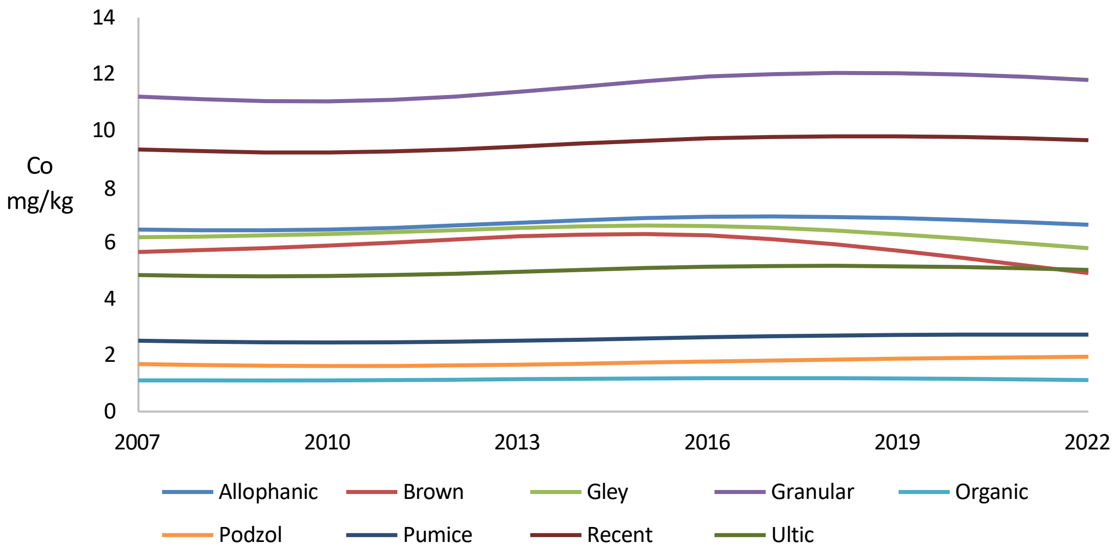

Figure 53. Change in mixed modelling average Co 2007-2022 by soil order.

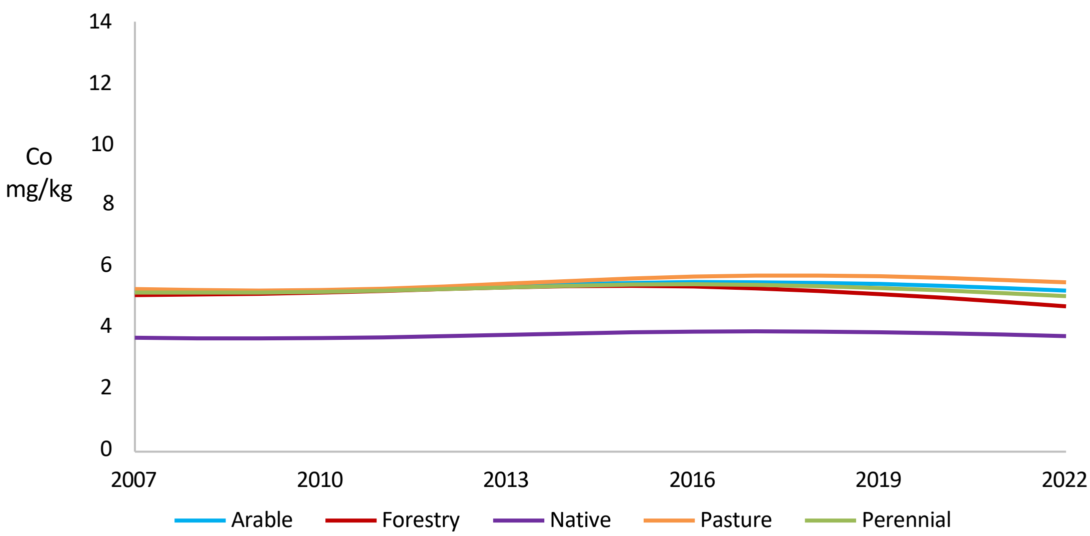

Figure 54. Change in mixed modelling average Co 2007-2022 by land use.

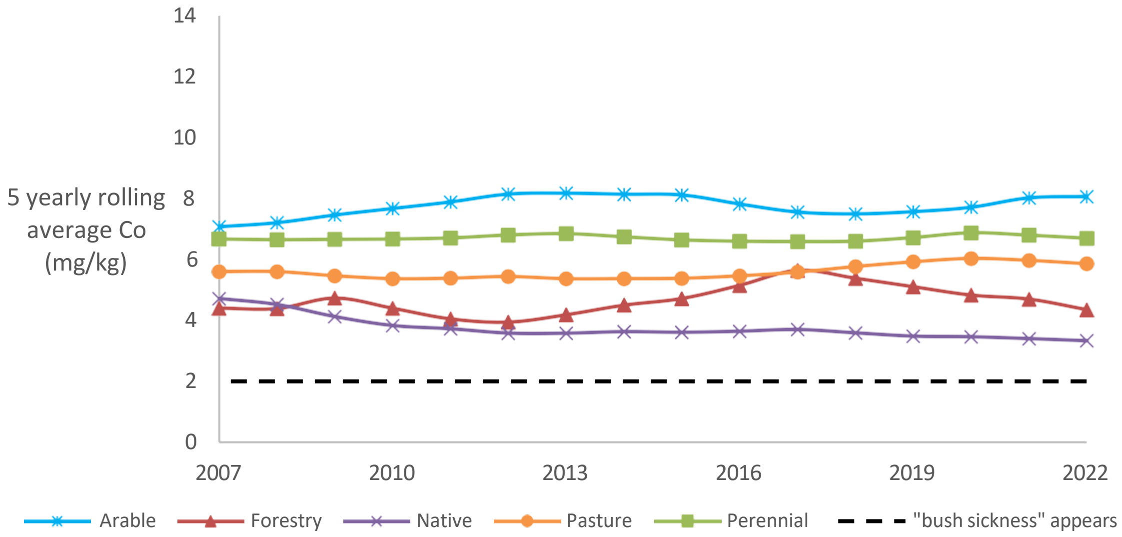

Figure 55. Average Co by land use 2007-2020. The dashed line indicates the level below which “bush sickness” could occur in stock (Hawke et al. 1994).

Molybdenum (Mo)

Molybdenum is considered essential for plants, mammals, some microorganisms and aquatic organisms, yet has complex interactions with soil pH, redox condition and other elements in soil. However, Mo requirement is relatively low, and it may become toxic at higher concentrations to plants, microorganisms (Kabata-Pendias & Murkherjee 2007; Chang & Page 2000) and to animals, even toxicity can appear at quite low concentrations (Gowariker et al. 2009).

Rhizobium bacteria and other N-fixing microorganisms have an especially large requirement for Mo, so Mo deficiency may be an issue for clover/ryegrass based pastoral systems. If plants are consistently low in Mo content, not only animals but human vegetarians may be at increased risk of molybdenosis (Steinnes 2009). In addition, the increased mobility of Mo as pH increases may be a concern as increasing soil pH is one of the most common practices of reducing the bioavailability of potentially toxic cations

A major source of Mo is the weathering of ferromagnesian, iron and manganese hydroxide minerals, while fertiliser additions are the major anthropogenic source in the Waikato region.

Waikato region soils, generally, have adequate Mo, except for parts of the West Coast district, which are inherently Mo deficient (Morton 2019; Sherrell and Metherell 1986). Soils from volcanic ash and Pumice Soils, generally, have higher Mo concentrations. Acidic soils, especially sands, and fibrous peat soils are, generally, Mo deficient (Gowariker et al. 2009). Solubility and availability of Mo to plants is largely controlled by soil pH and drainage conditions and its availability decreases with decreasing pH. Mo interacts with several other elements, including P, S, Zn, Fe and, most importantly, with Cu (Gowariker et al. 2009). Excess Mo can cause Cu deficiency at otherwise sufficient Cu levels (molybdenosis), whereas Cu toxicity may occur at relatively moderate Cu levels if the Mo intake is too low (Steinnes 2009).

There was no suitable New Zealand guideline for Mo and are very few guideline values internationally. No suitable guideline value for agricultural land was found so two overseas guideline values were considered. These were the Netherlands Remediation Urgency human health and ecological receptors guideline value for residential with <10% Produce consumption of 190 mg/kg (MIE 2009) and the USA Regional Screening Level protective of human health for Chemical Contaminants at Superfund Sites (US EPA regions 3, 6 and 9) for residential land of 390 mg/kg. In comparison, the highest Mo value measured at soil quality monitoring sites was 2.3 mg/kg, therefore excessive Mo is unlikely in the Waikato region.

The mixed modelling results showed there was a significant declining nonlinear trend, both overall (p=0.004, Figure 56) and by soil order (p=0.001, Figure 57). A decline in Mo combined with increases in Cu may result in Cu toxicity or molybdenosis for farm animals, plants and even humans.

There were no significant (p>0.05) changes in trend or pattern for Mo by land use (Figure 58), but there were significant differences (p<0.01) between land uses (Figure 58 and soil orders (Figure 57). Allophanic and Granular soils had higher concentrations than other soil orders, while Podzols, Pumice and Organic soils had the lowest concentrations.

Both mixed modelling and 5-yearly rolling average data (Figure 59) showed sites under arable and perennial had elevated concentrations of Mo compared with native sites. In this case, it seems soil order is more likely driving these higher concentrations. Mo is reported to be retained by soils on the surfaces of variable-charge minerals, such as Fe oxides in Granular soils (Evens and B. 2010), while Allophanic soils inherently have very high Anion Sorption Capacity. Arable and horticultural sites were dominated by these soil orders. Sites in forestry and pastoral land uses were close to native concentrations for both mixed modelling and 5-yearly rolling average data. Average concentrations of Mo are far below the Netherlands Intervention value, which is 190 mg/kg (MIE 2009).

Overall, Mo is declining in the Waikato region and, combined with increasing Cu, there is some risk of Mo-Cu imbalances affecting primary production. Further investigation of the impacts of Mo deficiency on soil quality, particularly on soil ecology and biodiversity, should be carried out.

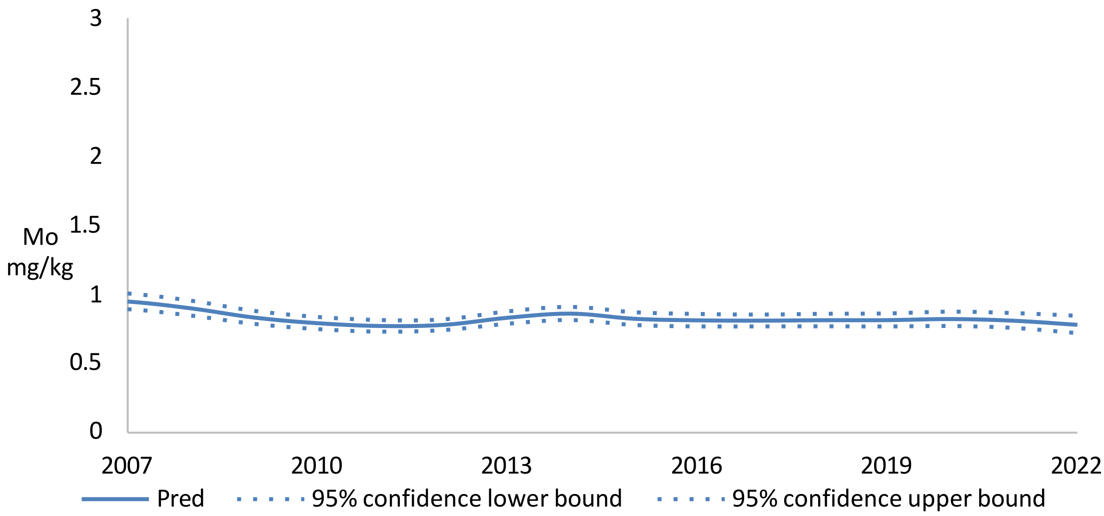

Figure 56. Change in mixed modelling average Mo concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

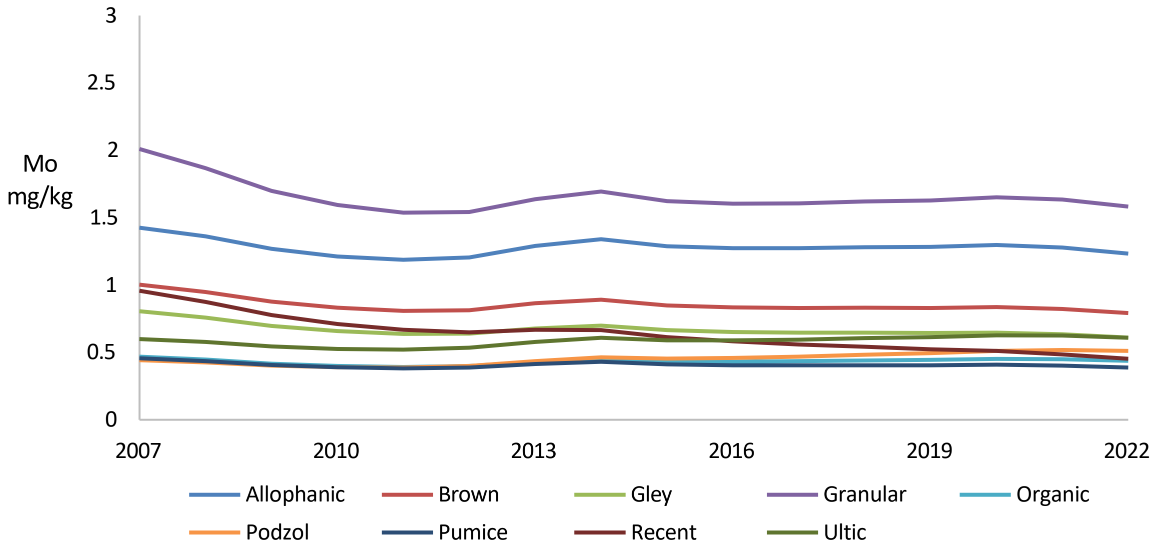

Figure 57. Change in mixed modelling average Mo 2007-2022 by soil order

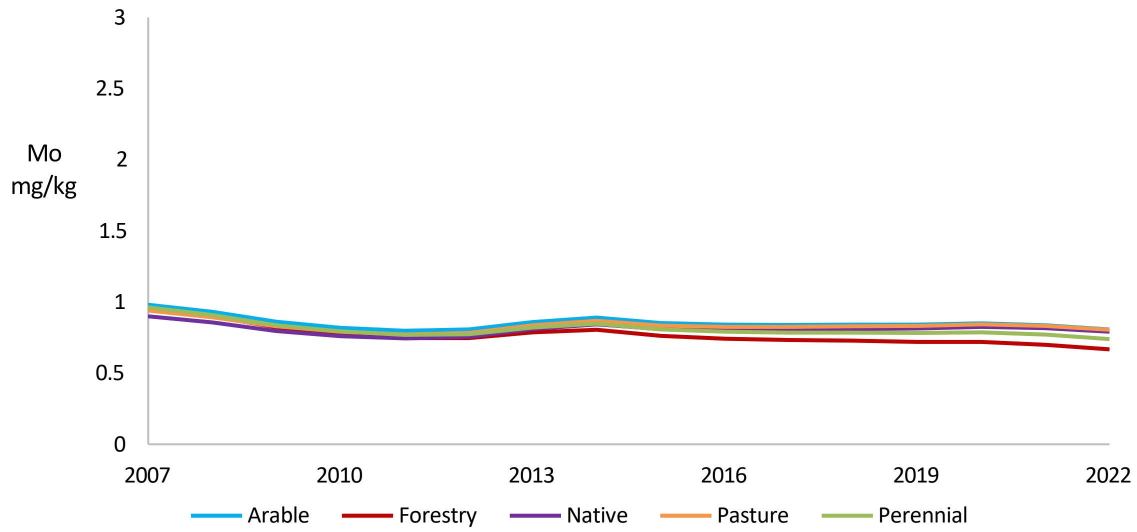

Figure 58. Change in mixed modelling average Mo 2007-2022 by land use.

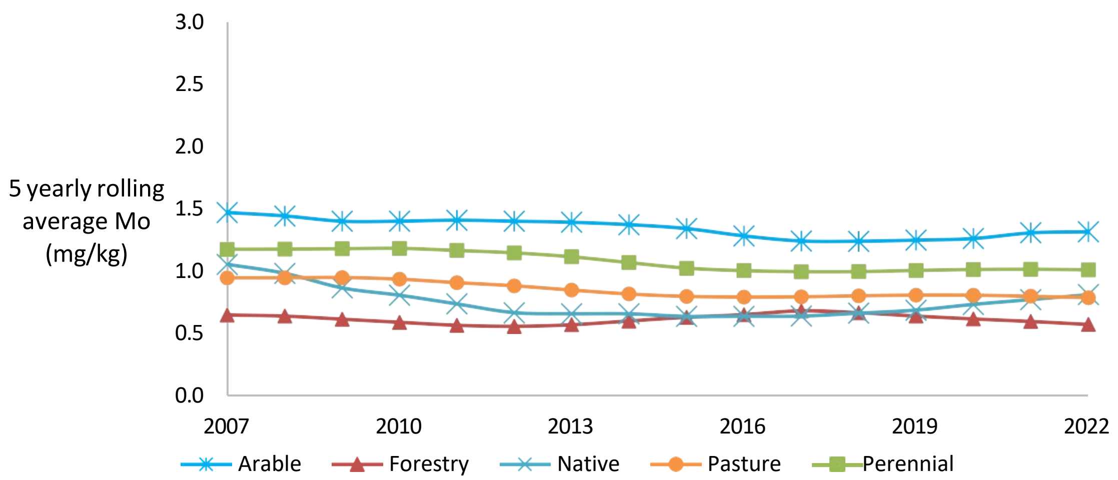

Figure 59. Average Mo by land use 2007-2022. The Netherlands Intervention value is 190 mg/kg (MIE 2009).

Antimony (Sb)

There is very little difference in Sb content between sites in native or other land uses, suggesting current deposition of Sb is minor. An interesting issue that arose were outlier values in soils from historic, often unrecorded, rifle ranges, where Sb and Pb concentrations were 100-fold higher than usual. These outliers were excluded from analysis although results proved useful for identifying and locating lost or unknown rifle ranges.

Currently, Sb is considered very toxic with no known use in biological tissue or processes. It shares many of the same chemical properties as arsenic (As) and is also chemically like phosphorous (P), which enables Sb to use P uptake mechanisms to enter biota. Toxic effects of Sb include respiratory and cutaneous effects, effects on the cardiovascular system, renal tubular acidosis, thrombocytopenia, and pancreatitis (Arai, 2010). It is a potential carcinogen and has an inhibitory role in DNA replication and metabolic processes (Wilson et al. 2010). However, the mechanism of toxicity of Sb compounds and the impacts of excessive Sb on the wider environment is not clearly understood, there is little information available on the transformation and transport of Sb in the different environmental compartments, all of which hinders the understanding behaviour and fate of Sb (Filella et al. 2002).

It is readily mobilised from background rocks by hydrothermal waters, and some is transported to hot springs and near-surface geothermal systems in the Waikato region, accompanying As and Hg (Craw 2008). Antimony was widely used for thousands of years in gold extraction, cosmetics and, more recently, in insecticides. Possible Sb-containing insecticides used in the Waikato include antimony potassium tartrate and lead arsenate, where Sb is an impurity (about 1%). Antimony is also used in primer for firearms and is as an alloy with Pb in tyre balance weights (Taylor & Kruger 2020). Taylor & Kruger (2020) estimated about 760 kg of Sb are deposited on urban roads in New Zealand annually. However, deposition from tyre weights to the rural environment are expected to be much less.

There was no suitable New Zealand guideline value for Sb and are very few guideline values internationally. Also, no suitable guideline value for agricultural land was found. Three overseas guideline values were considered. These were The Netherlands Remediation Urgency human health and ecological receptors guideline for residential land with <10% Produce consumption for Sb of 22 mg/kg (MIE 2009), the USA Ecological Soil Screening Level for Sb protective of ecological receptors (US EPA 2005) of 78 mg/kg, and the Regional Screening Levels protective of human health for Chemical Contaminants at Superfund Sites (US EPA regions 3, 6 and 9) for residential land of 31 mg/kg. No soil quality monitoring sites exceeded any of these guideline values.

The mixed modelling results showed no significant ($p>0.05$) change in average Sb for the overall data (Figure 60) and there was no significant ($p>0.05$) change in trend or pattern for average Sb by soil order (Figure 61) or land use (Figure 62). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Allophanic and Granular soils consistently had higher average Sb levels, while Podzols, Ultic and Brown soils consistently had lower average Sb levels. Similarly, perennial consistently had higher average Sb levels, while forestry, pasture and native soils consistently had lower levels. The loss of sites in long-term vineyard or berry production to urban sprawl also impacted average values as these sites had about 3-fold higher Sb values than the average. Insecticides containing Sb may have been used at these sites as no other source for Sb at these sites could be found. As a result of the loss of sites with higher Sb, differences between land uses have decreased over time.

Nevertheless, Sb concentrations in soils of the region are low overall and there is no current increasing trend (Figure 63). Sites under native land use can be taken as indicative of background values, i.e. as if the soil was unimpacted by human activities. In 2020, there is very little difference between sites in native or other land uses, suggesting current deposition of Sb is minor (Figure 64).

Allophanic soils have high anion holding capacity, while Granular soils have high concentrations of iron minerals that can similarly bind to some anions, suggesting these soils have naturally higher Sb than Podzols Ultic and Brown soils. Horticultural land uses currently monitored (i.e. excluding sites lost to urban sprawl) are relatively young (established since the 1970's) so have not received Sb-containing insecticides, yet still appear to have elevated Sb, suggesting the higher Sb here is natural.

Once old rifle ranges were excluded, one other site was clearly elevated compared to the remaining sites. This site is an urban park planted in indigenous forest that was historically part of a horse racing club and the site of the Agricultural and Pastoral Association shows. By 1928, when it was gifted to Hamilton City, it had been depleted by logging (since the 1860's) and extensively damaged by cattle (HCC 1993). Although concurrent high Pb levels suggest the extensive use of firearms or vehicle tyre weights as the source of Sb, the use of Sb-containing insecticides to control pasture pests at this site cannot be excluded. Even though this site was in indigenous forest over 150 years old, the historic impact of man on this site was quite evident in soil quality measurements.

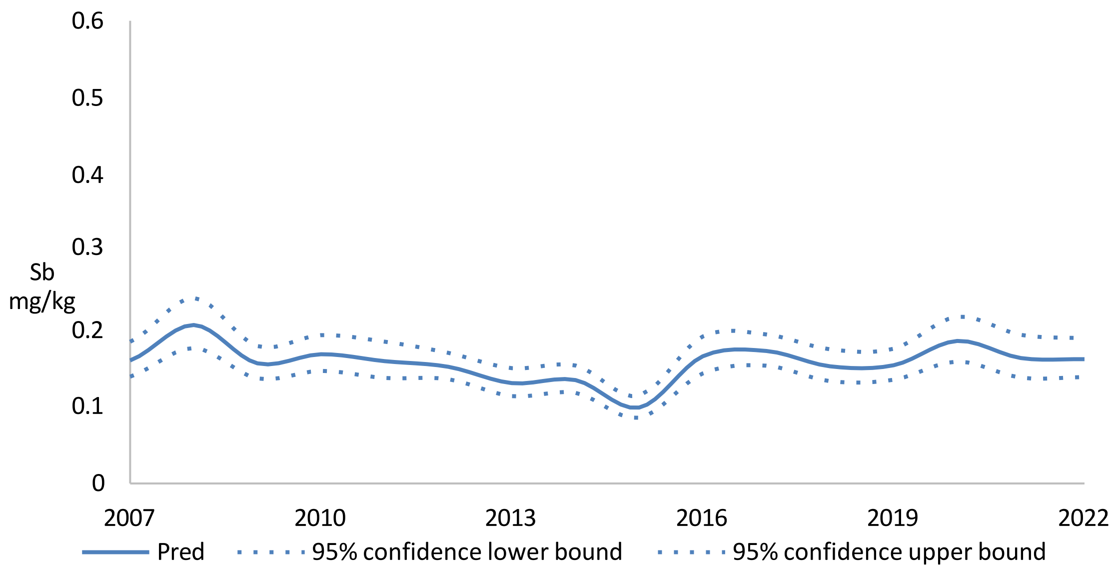

Figure 60. Change in mixed modelling average Sb concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

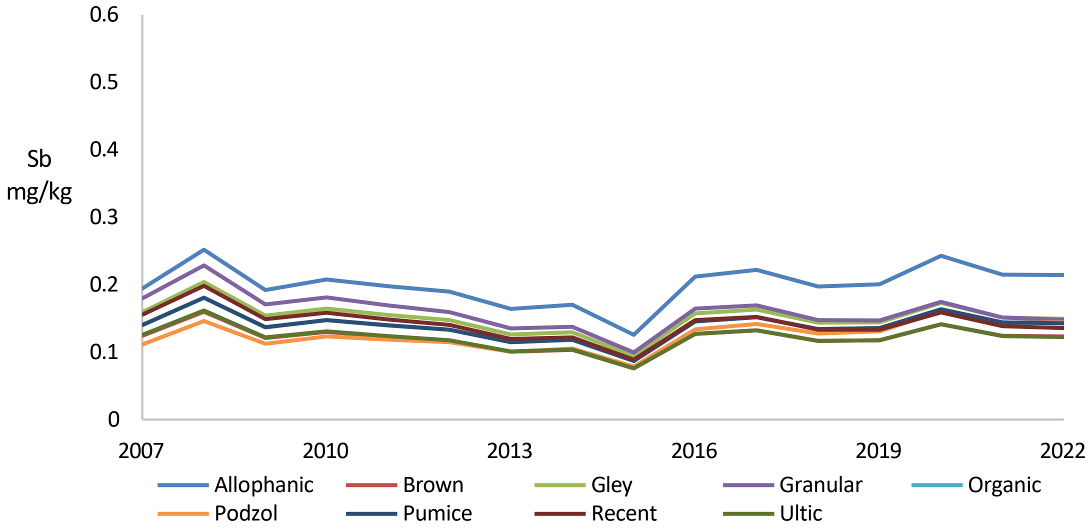

Figure 61. Change in mixed modelling average Sb 2007-2022 by soil order.

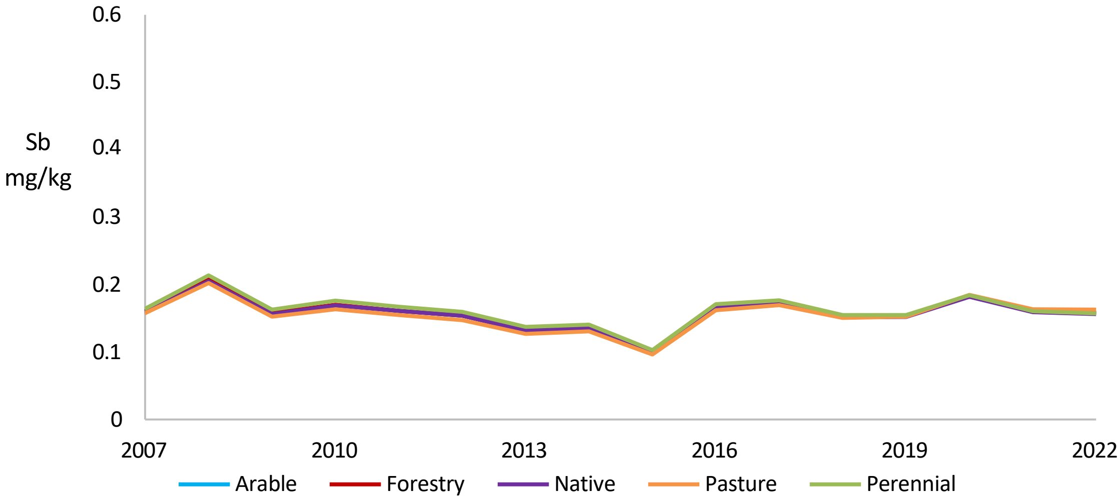

Figure 62. Change in mixed modelling average Sb 2007-2022 by land use.

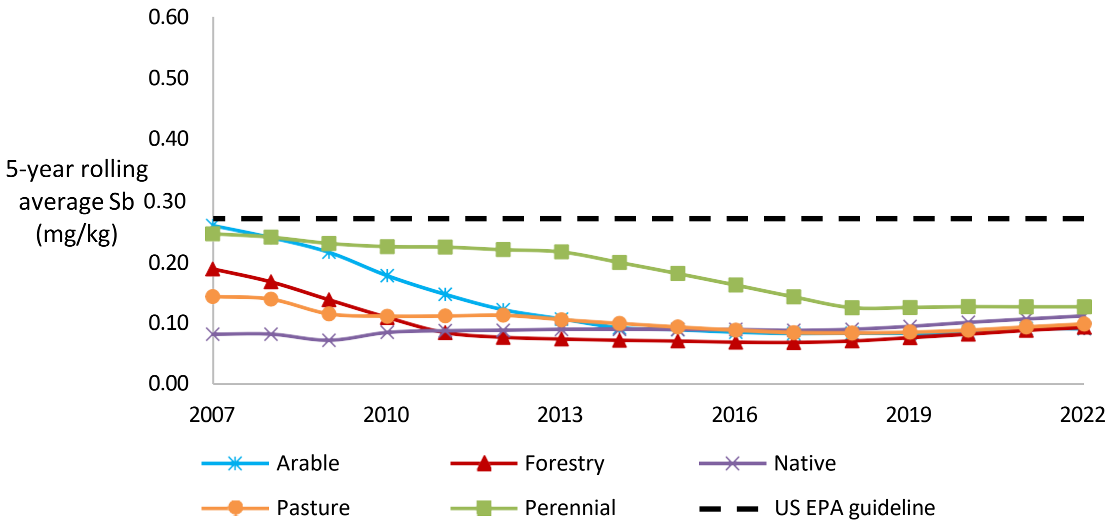

Figure 63. Average Sb by land use 2007-2022. The guideline is the US EPA ecological screening level for the protection of mammalian species (USEPA 2012).

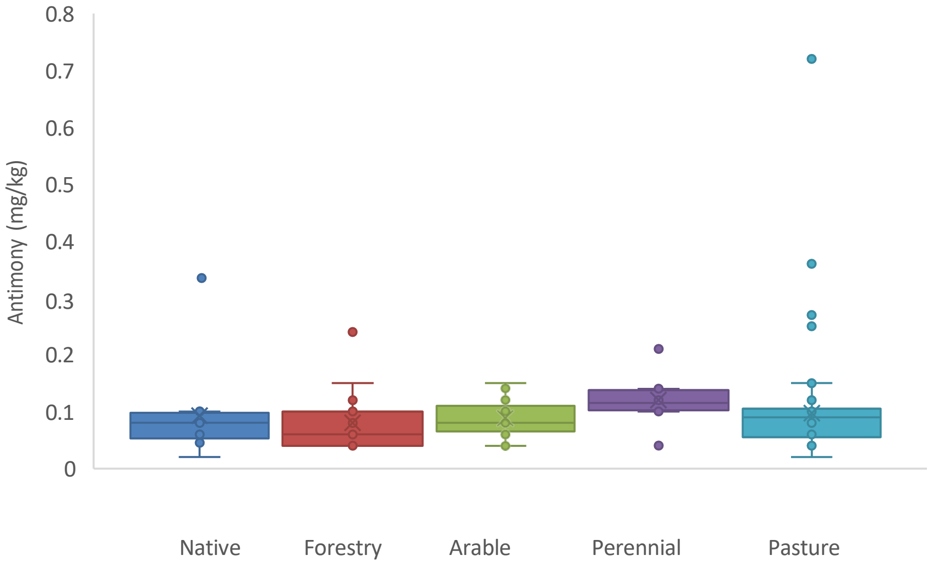

Figure 64. Boxpots of acid recoverable Sb (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region. One arable site with Sb of 11.1 mg/kg not shown

Mercury (Hg)

Mercury is considered nonessential, toxic and bioaccumulative. It has no known vital biological functions and can be toxic to virtually all forms of life and is a priority contaminant for resource managers (Kim & Taylor 2013, MfE 2011). It is unique in that it exists or is found in nature in three forms: elemental, inorganic, and organic (Tchounwou et al. 2012). All three forms of Hg can have acute or chronic effects on humans and other higher animals including irreversibly damage to the central nervous system, cancer, intestinal disturbances, and death (Tchounwou et al. 2012, Clifford et al. 2010).

Sources of Hg in the Waikato include burning fossil fuels, volcanic emissions, geothermal power generation, impurities in fertilisers, dentistry, industrial wastes, and sewage, while past sources of Hg are pesticides, gold and silver mining (Tchounwou et al. 2012, Clifford et al. 2010). Although most of these sources are localised, volcanic emissions contribute about 20-40 % of global emissions (Pyle & Mather 2002) and are potentially a major source of Hg to Waikato soils.

The New Zealand Soil Contaminant Standard using the rural residential scenario for Hg is 200 mg/kg (MfE 2011). In comparison, the Canadian soil guideline value for agricultural soils for the Protection of Environmental and Human Health is 6.6 mg/kg (CCME 1999), while the USA EPA Supplemental Guidance for Developing Soil Screening Levels at Superfund Sites (US EPA, 2002) human health guideline protective of Hg leaching to groundwater was 2 mg/kg. No soil quality monitoring sites exceeded any of these soil guideline values.

The mixed modelling results showed no significant trend overall ($p>0.05$), (Figure 65). There were no significant ($p>0.05$) changes in trend or pattern for Pb by soil order (Figure 66) or land use (Figure 67). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Allophanic and Granular soils had higher average concentrations of Hg than other soil orders, while Pumice soils had very low concentrations. Nevertheless, differences in Hg content between sites in native or other land uses are low and not significant, suggesting current deposition of Hg is low (Figures 68-69).

Mixed modelling calculated results showed average Hg for the perennial land use was noticeably higher than other land uses although this differed from the 5-year rolling average results where perennial was similar to other land uses and arable average Hg was higher (Figures 66-67). Possible sources of Hg include impurities in fertilisers and Hg-base pesticides. Zheng et al. (2008) reported fertiliser application influenced soil Hg concentrations at a long-term experimental station with naturally low soil Hg, while Mirlean et al. (2008) found Hg concentrations in soil close to a fertiliser factory were up to 32 times those for background soils. The use of Hg-based fungicides and seed coatings were banned in the 1970's (Clifford et al. 2010). If historic fungicides and seed coatings were the source of the enriched Hg, it would mean Hg is strongly held onto the soil and relatively immobile.

However, the effects from Hg concentrations in produce grown on these horticultural/arable sites are likely to be minor as the availability of soil-bound Hg to plants is usually low and mostly accumulates in the plant roots (Tyler 2004b, McLaughlin et al. 1996). Plant capacity to take up Hg varies, e.g. some plant species, such as lichens, carrots and lettuce, are likely to take up more Hg than other plants grown at the same sites (Kabata-Pendias & Mukherjee 2007). Fungi also vary in their ability to take up Hg; Falandysz et al. (2007) found King Bolete mushrooms (Boletus edulis) had accumulated up to 130 and 72 mg/kg in caps and stalks, respectively.

Consistent with the lack of a clear trend of Hg accumulating in soil, estimate of aerial deposition are quite low. The likelihood of errors decreases if estimates can be made comparing several different methods, as present below. Estimates of Hg deposition in NZ peat bogs were attempted by Lamborg et al. (2002), which gave Hg accumulation rates uncorrected for peat accumulation/decomposition ranging from about 1-40 $\mu g/m^2/y$. This result appeared collaborated by the Pb^{210} corrected accumulation rates in NZ lakes, which ranged from 2-47 $\mu g/m^2/y$ (Lamborg et al. 2002). Accumulation rates for Hg in countries of similar latitude could be expected to be similar, so Chile and Canada should be suitable proxies for NZ. Accumulation rates for Hg of about 1-7.9 $\mu g/m^2/y$ were measured in Chilean peat bogs (Hermanns & Biester 2013, Biester et al. 2002a, 2003). The lower rates are the historic background, while the higher rates reflect modern global Hg deposition. Rates in rain collections and accumulation rates in bogs and lakes of 8, 8 and 11 $\mu g\ Hg/m^2/y$, respectively, were measured in Nova Scotia, Canada (Lamborg et al. 2002). Based on these measurements using different methods, it will take thousands of years to have any significant impact on soil concentrations assuming accumulation rates remain constant, and no Hg is lost from soil.

However, accumulation rates so estimated may be prone to considerable uncertainty technical difficulties with correcting for the contributions of location, climate, localised sources such as volcanic eruptions, catchment effects such as erosion and deposition, sediment focusing, preferential mobilisation and transport of Hg, in-lake productivity, peat growth/degradation rates and smearing of Pb^{210} concentrations which are used in dating peat (Hermanns & Biester 2013a, Biester et al. 2007, Biester et al. 2003). Lamborg et al. (2002) were unable to accurately date the peat layers in their study. As an aside, tephrachronology of volcanic ash layers common in NZ peat bogs could be utilised to provide dates in such studies (Lowe et al. 2008).

As trends are not consistent and Hg is a potential highly toxic contaminant, monitoring and assessment of Hg should continue to provide early warning of any negative environmental or human health effects.

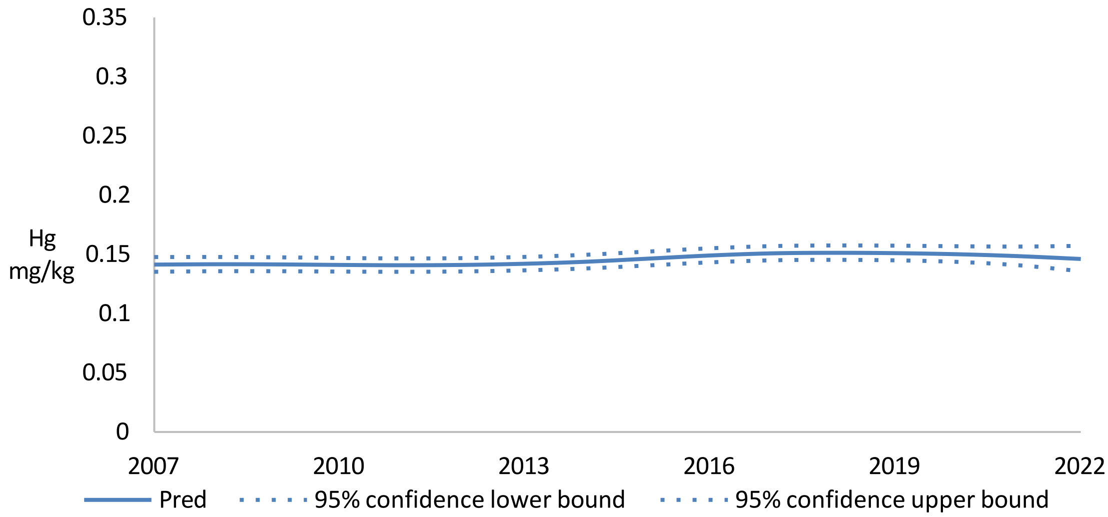

Figure 65. Change in mixed modelling average Hg concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

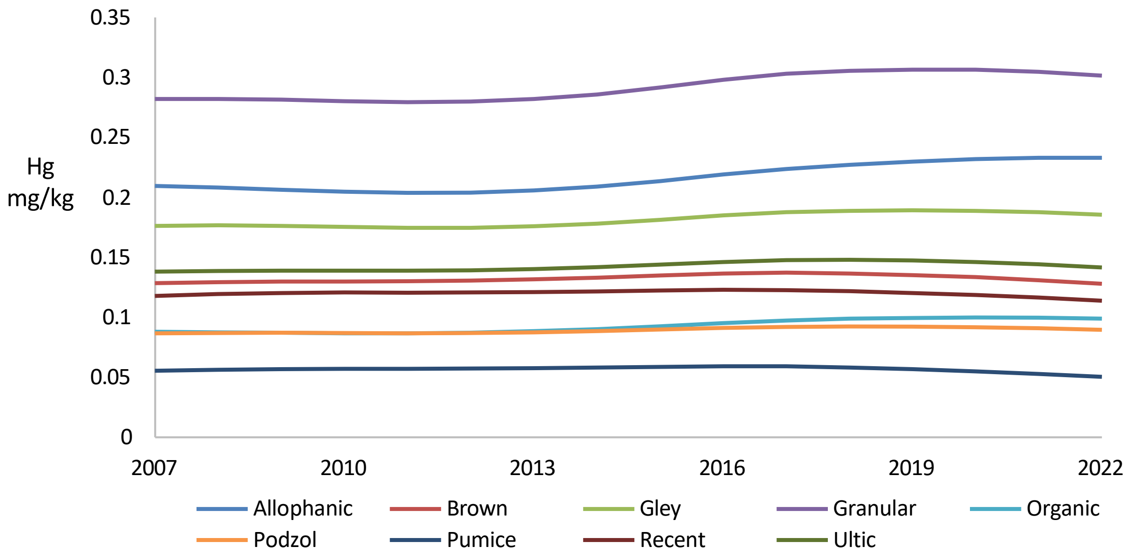

Figure 66. Change in mixed modelling average Hg 2007-2022 by soil order

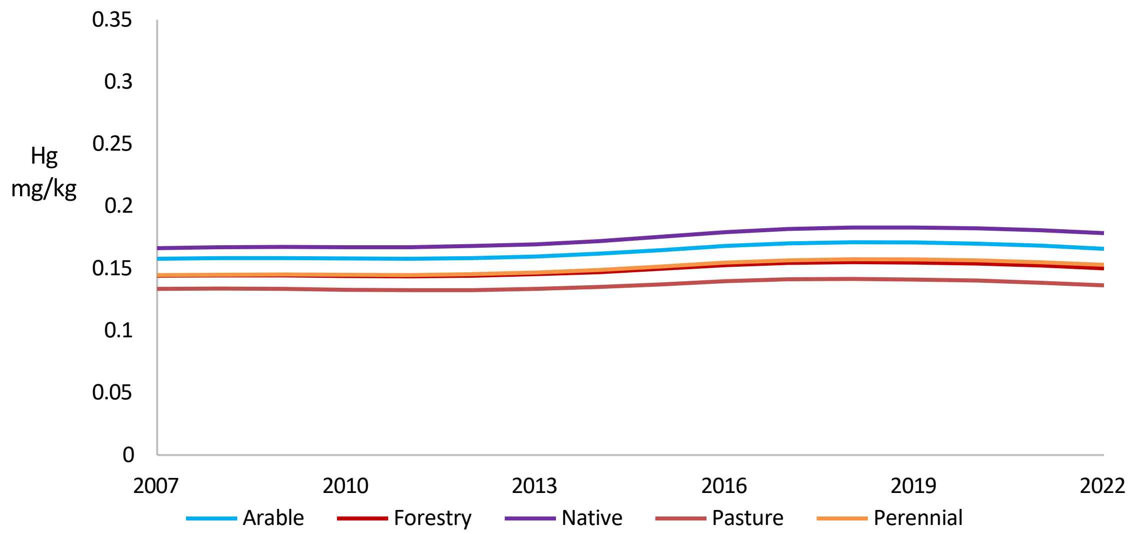

Figure 67. Change in mixed modelling average Hg 2007-2022 by land use.

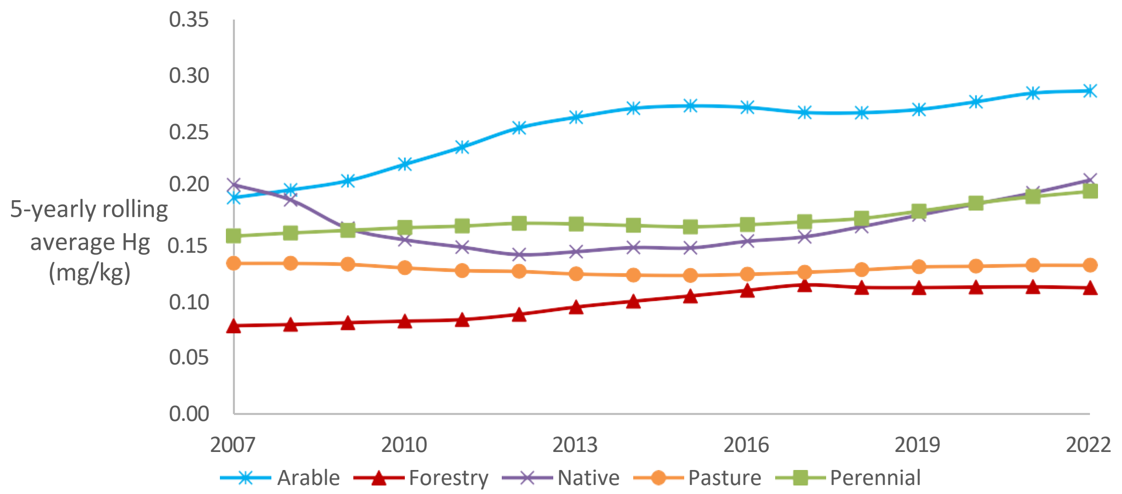

Figure 68. Average Hg by land use 2007-2022. The Canadian Soil Quality Guideline soil guideline value for Hg for agricultural soils for the Protection of Environmental and Human Health is 6.6 mg/kg (Canadian Council of Ministers of the Environment, 1999).

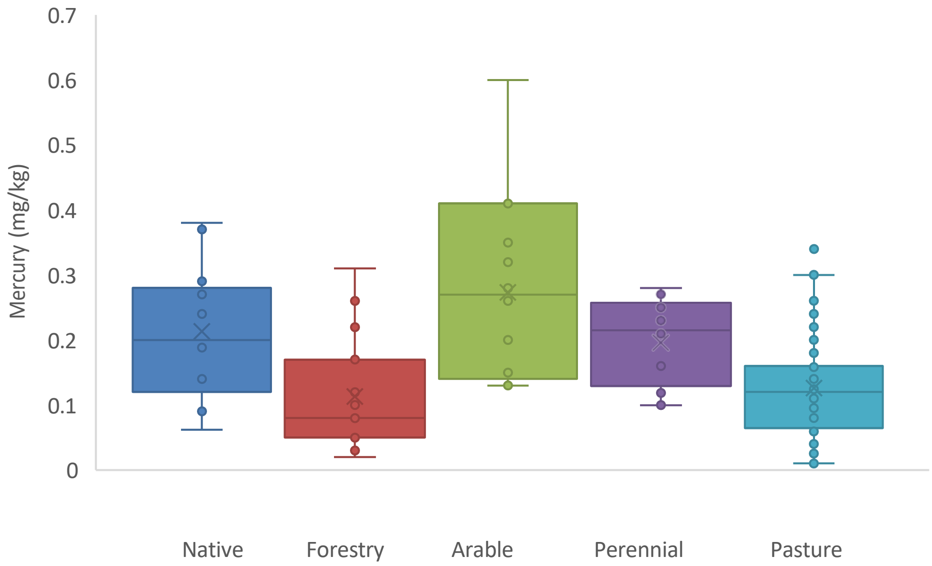

Figure 69. Boxpots of acid recoverable Hg (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Silver (Ag)

Perennial land use had higher average Ag concentrations compared to native and all other land uses. These high concentrations were driven by high concentrations found at historic apple orchards.

As Ag is so highly toxic to bacteria, it is used in medicine as a bactericide and a fungicide (Drake & Hazelwood 2005). However, Ag is not known as a systemic toxin to humans and other higher animals except at extreme doses, where compounds can be absorbed by body tissues causing consequent bluish or blackish skin pigmentation (argiria) or eyes (argyrosis). Terrestrial species can also be adversely affected by Ag. Earthworms had reduced growth in soil with 62 mg kg^{-1} Ag_2S, a relatively insoluble and less toxic Ag compound (Ewell et al. 1993, quoted in Kabata-Pendias & Mukherjee 2007). Nitrifying bacteria in the soil were inhibited at concentrations 540 - 2700 mg Ag kg^{-1} (Choi & Hu 2008).

Although Ag has not commonly been considered an environmentally important metal, it has become increasingly used as antimicrobials in consumer products used in the Waikato region (e.g. liquid soaps, sunscreens) and antibiotics (Lorenz et al. 2011). Ag nanoparticles are included in clothing, paints, food containers, automobiles, building materials and medical equipment

(Evans & Barabash 2010). Other sources of Ag in the Waikato region can include emissions from the imaging industry, electronics and coal combustion (WHO 2002).

There are no New Zealand risk-based guideline values for Ag. Overseas guideline values include the US EPA Regional Screening Level for Ag protective of human health for Chemical Contaminants at Superfund Sites for residential land of 390 mg/kg (USEPA 2002); the Netherlands Remediation Urgency human health and ecological receptors guideline value for residential land with <10% Produce consumption of 15 mg/kg (MIE 2009); the USEPA ecological screening levels for silver protective of ecological receptors, avian species, and mammalian species of 560 mg/kg, of 4.2 and 14, respectively; and the USEPA soil screening level protective of groundwater for Ag of 2 mg/kg. No soil quality site exceeded any of these guideline values.

The mixed modelling results showed there was a significant (p=0.034) decreasing nonlinear decreasing trend overall (p=0.034, Figure 70) and in land use (p=0.038), but there were no significant (p>0.05) changes in trend or pattern for Ag by soil order. However, there were significant differences between land uses (p<0.01) and soil orders (P<0.01). Granular and Allophanic soils had higher average Ag concentrations than other soil orders, while Organic, Pumice and Ultic soils had the lowest average concentrations (Figure 71). Perennial land use had higher average Ag concentrations compared to native and all other land uses (Figures 72-74). These high concentrations were driven by high concentrations found at old apple orchards. More recent lower Ag concentrations can be explained by increased numbers of kiwifruit orchards in the region, while historic apple orchards with high Ag concentrations were progressively converted to other land uses with inversion and mixing of the surface soil resulting in diluting and burying of historic Ag (Figure 75).

However, average concentrations are extremely low (<0.04 mg/kg measured for perennial) and there appears no current issue with Ag in the Waikato region.

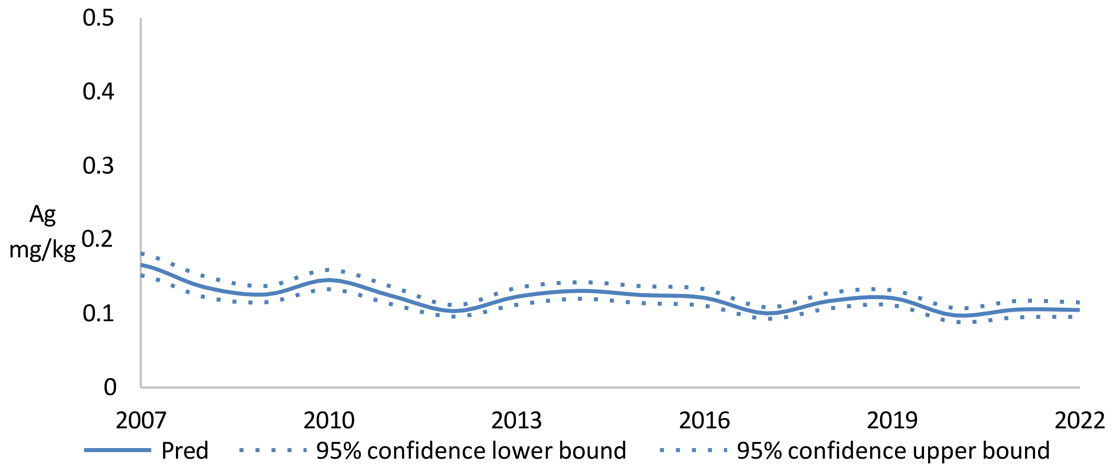

Figure 70. Change in mixed modelling average Ag concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

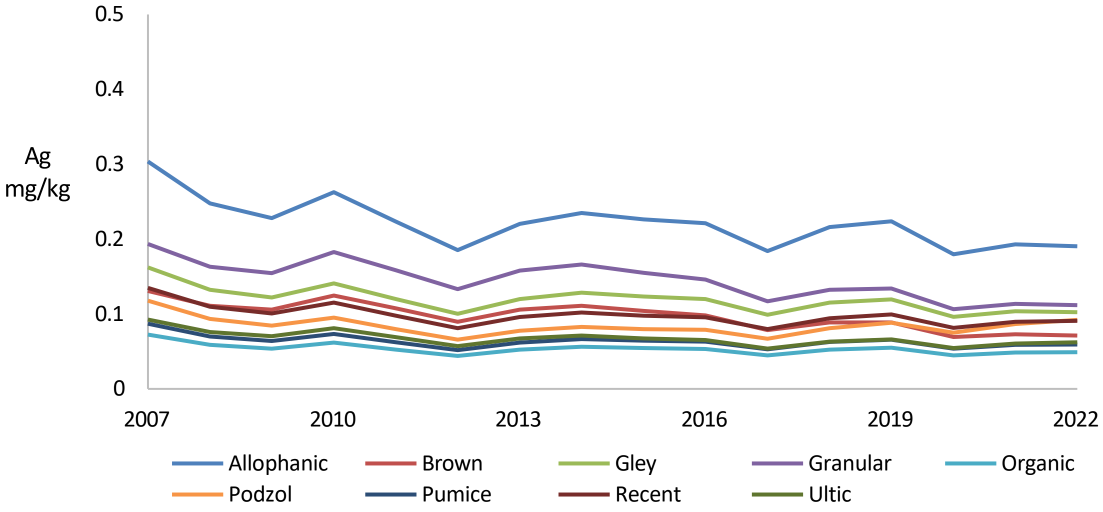

Figure 71. Change in mixed modelling average Ag 2007-2022 by soil order.

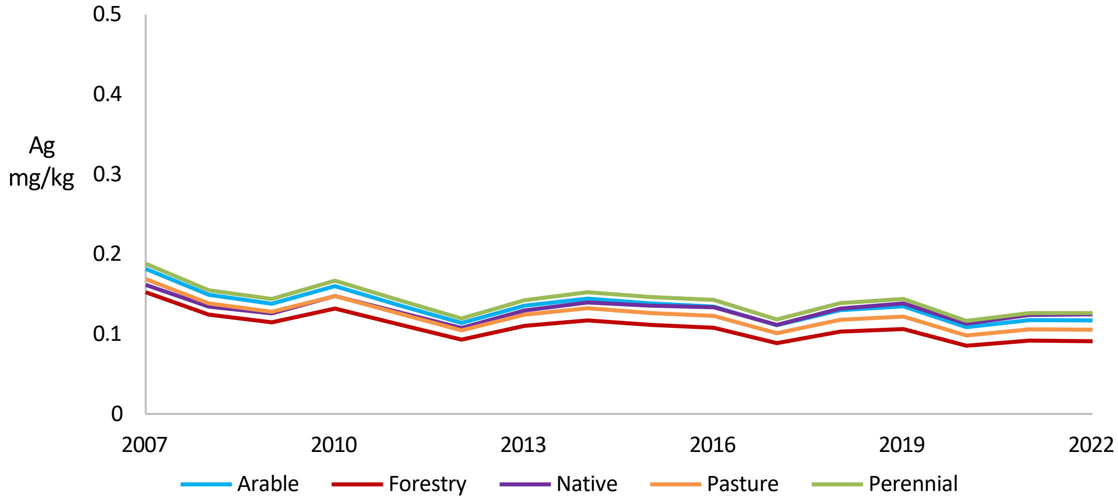

Figure 72. Change in mixed modelling average Ag 2007-2022 by land use.

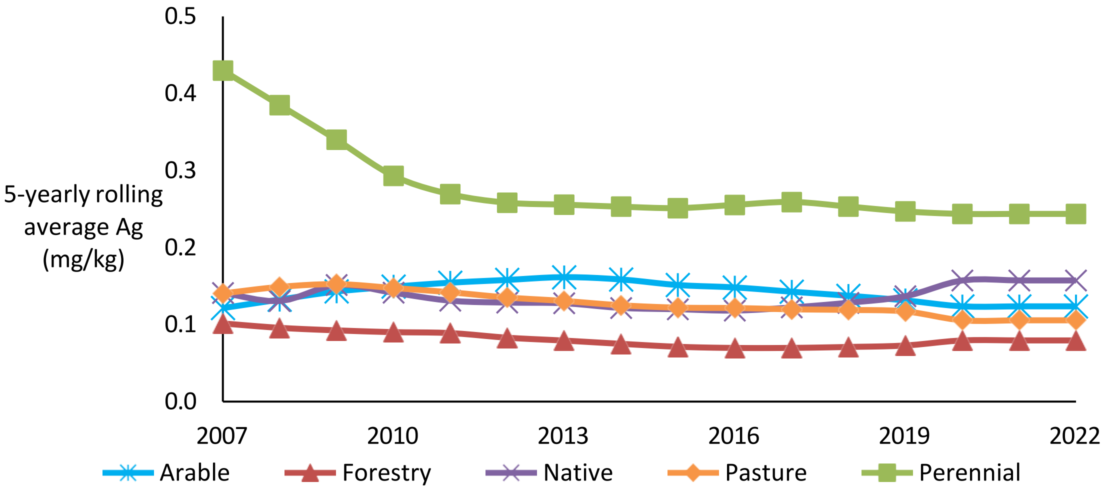

Figure 73. Average Ag by land use 2007-2022. In comparison, the Netherlands Remediation Urgency human health and ecological receptors guideline value for residential land with <10% Produce consumption is 15 mg/kg (MIE 2009).

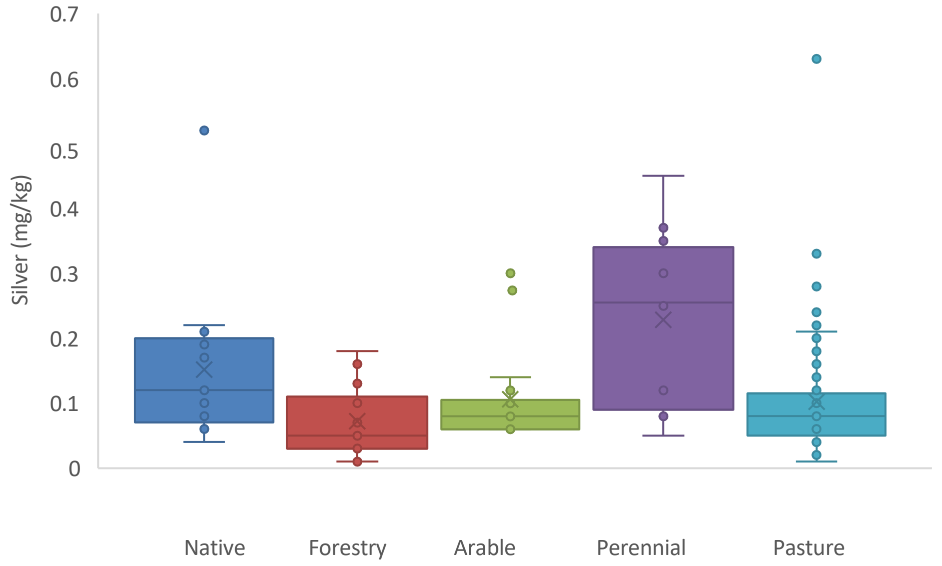

Figure 74. Boxpots of acid recoverable Ag (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Figure 75. Removal of old apple trees to make way for kiwifruit inverts and mixes soil.

Thallium (Tl)

Thallium is a non-essential and potentially highly toxic element, comparable to cyanide, that appears on the list of USEPA (2015) priority pollutants (http://www2.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf) and the European Water Framework Directive (2000). Its average crustal abundance is about 0.7-0.8 mg/kg (Evans & Barabash 2010; LaCoste et al. 2001) and is chemically like K and of a similar size. Thus, Tl can replace K in micas and feldspars (Belzile and Chen 2017; Temel et al. 1997). It is not strongly bound by soil constituents and can quickly de-sorb, so poses a potential environmental and health risk. It is likely to have been used in the Waikato region as a rodenticide although Tl's use was restricted in 1965 in the United States, and the World Health Organization (WHO) recommended in 1973 against its use due to its toxicity (WHO, 1973). Recent dietary exposure assessment has demonstrated that Tl can exceed the health-based guidance value for infants in the New Zealand diet (Pearson & Ashmore 2020). In addition, accumulation of natural soil thallium in brassica species has been reported following an event in California involving poisoning of a family from kale vegetable chips. So, monitoring for Tl has taken on new significance.

Pesticides and the electronics industry are common sources of Tl. It has been used in rat and ant poisons, for semiconductors, switches and fuses, added to glass to increase its density and refractive index, and radioactive Tl compounds are used in medical applications (Evans & Barabash 2010; LaCoste et al. 2001). Although there is very little manufacture in the Waikato region, many of these products have been imported and the waste of such product may be a future source of contamination.

As Tl can substitute for K, applications of potassium fertilisers are a likely source. Consistent with this hypothesis, Tl levels have been found to increase in garden plants treated repeatedly potash fertilisers (Viraraghavan and Srinivasan 2011). Although Tl in potassic fertilisers were found to usually be low, <0.1 mg/kg, some phosphate fertilisers were found to have higher Tl concentrations and may be a more significant source (Taylor 2016; Temel et al. Zartner-Nyilas, 1987.

There are no New Zealand risk-based guideline values for Tl. The risk-based overseas guideline value from the Canadian Soil Quality Guideline for Tl for the Protection of Environmental and Human Health on agricultural land of 1 mg Tl/kg soil was identified (CCME 1999).

The mixed modelling results showed there was a no significant trend overall ($p>0.05$, Figure 76) and there were no significant ($p>0.05$) changes in trend or pattern for Tl by soil order (Figure 77) or land use (Figure 78). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Granular and Allophanic soils had higher average Tl concentrations than other soil orders, while Podzols, Pumice and Organic soils had the lowest average concentrations. The higher concentrations of Tl are consistent with Tl adsorbing onto clay minerals and iron oxides found in these soils (Zhuang et al. 2021, Lin et al. 2021). Perennial and arable land uses had higher average Tl concentrations compared to native, pasture and forestry land uses (Figures 13 & 79). These results are consistent with the past use of Tl-containing pesticides on horticultural and arable land. However, it is not clear if there are current diffuse sources of Tl to Waikato soils.

Although average Tl concentrations were below the guideline value, individual sites under arable, perennial and a goat farm site receiving animal effluent exceeded the guideline for the Protection of Environmental and Human Health (CCME 1999). Understanding if Tl is an emerging issue is desirable as is developing a New Zealand risk-based guideline. Overall, a watch should be kept on Tl.

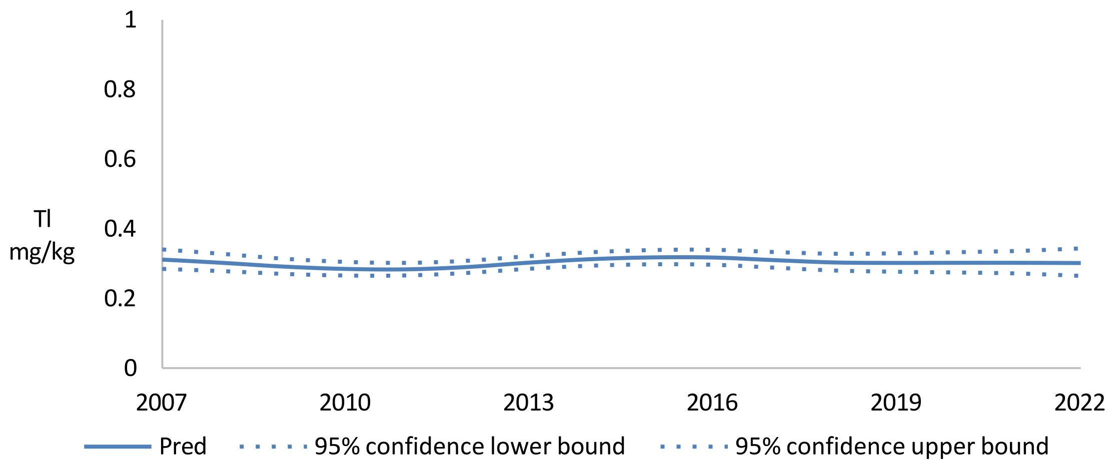

Figure 76. Change in mixed modelling average Tl concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

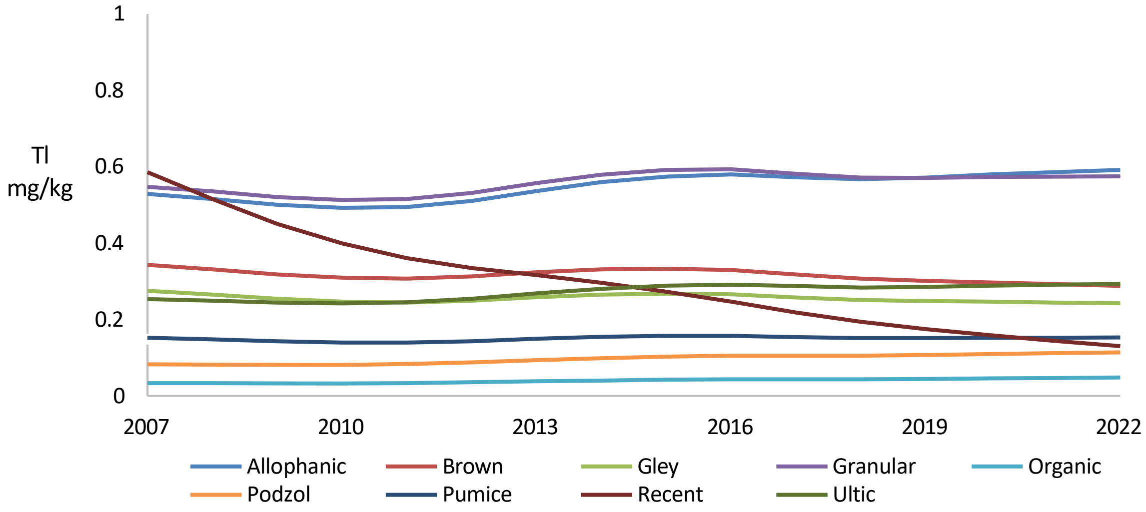

Figure 77. Change in mixed modelling average Tl 2007-2022 by soil order.

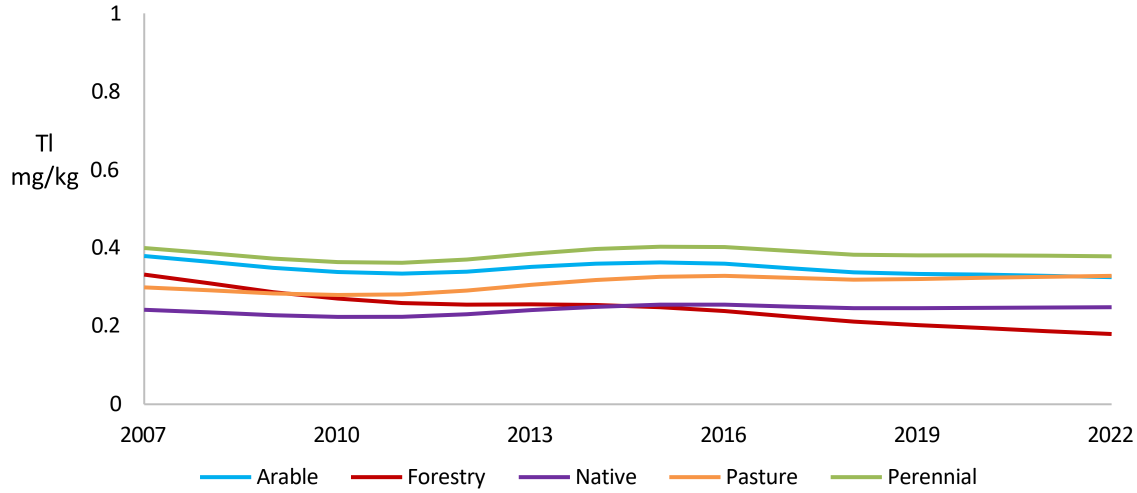

Figure 78. Change in mixed modelling average Tl 2007-2022 by land use.

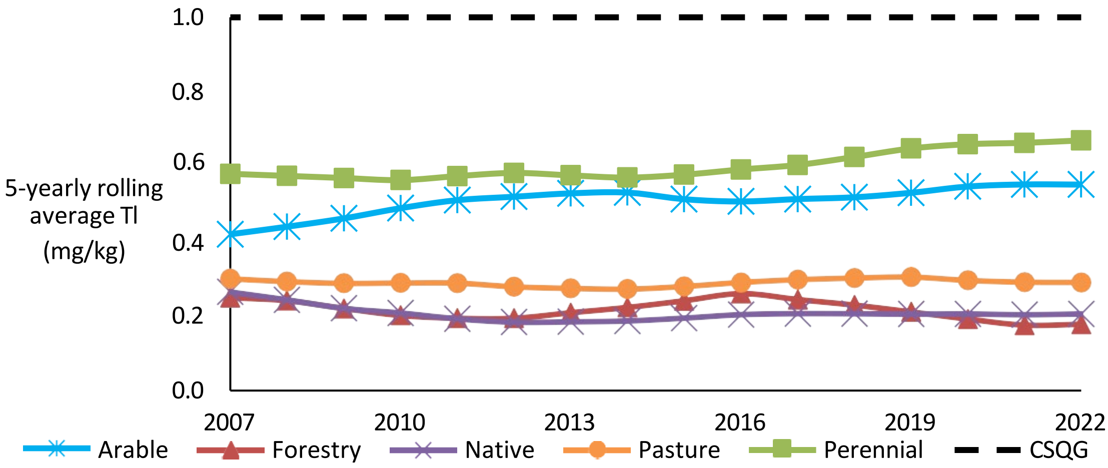

Figure 79. Average Tl by land use 2007-2020. The Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health for Tl is 1 mg/kg.

Tin (Sn)

Inorganic Sn is thought to have low toxicity, but organic Sn is potentially highly toxic and can affect liver and brain function, damage chromosomes, red blood cell production and the immune system (Cima 2011, Clifford et al. 2010). The dominant source of Sn contamination overseas is smelters, with lesser sources including metal coatings, paint and plastic additives, pesticides, and burning of fossil fuels. It is these lesser sources that are likely to contribute Sn to the Waikato region. Nevertheless, due to the lack of Sn smelting in New Zealand, Sn is expected to be of low environmental significance in the region.

There are no New Zealand risk-based guideline values for Sn. The overseas guideline from the Netherlands intervention value was identified (900 mg/kg). The magnitude of Sn measured in soils in the Waikato region were 2-3 orders of magnitude below the Netherlands intervention value.

The mixed modelling results showed there was a non-significant nonlinear trend overall ($p>0.05$, Figure 80). However, there were significant differences in trend for Sn by soil order ($p=0.017$ Figure 81) and between land uses ($p<0.01$) and soil orders ($P<0.01$), but there were no significant ($p>0.05$) changes in trend or pattern by land use (Figure 82). The curves derived for each soil order differed remarkably in their shape. Granular and Allophanic soils had higher average Sn concentrations than other soil orders, while Podzols, Pumice and Ultic soils had the lowest average concentrations. Perennial and arable land uses had slightly higher average Sn concentrations compared to native, pasture and forestry land uses (Figures 83 & 84).

Overall, Sn abundance in soils of the Waikato region is so close to the detection limit that sampling and analytical errors are probably confounding interpretation of the results and no issue with Sn in the Waikato region was identified.

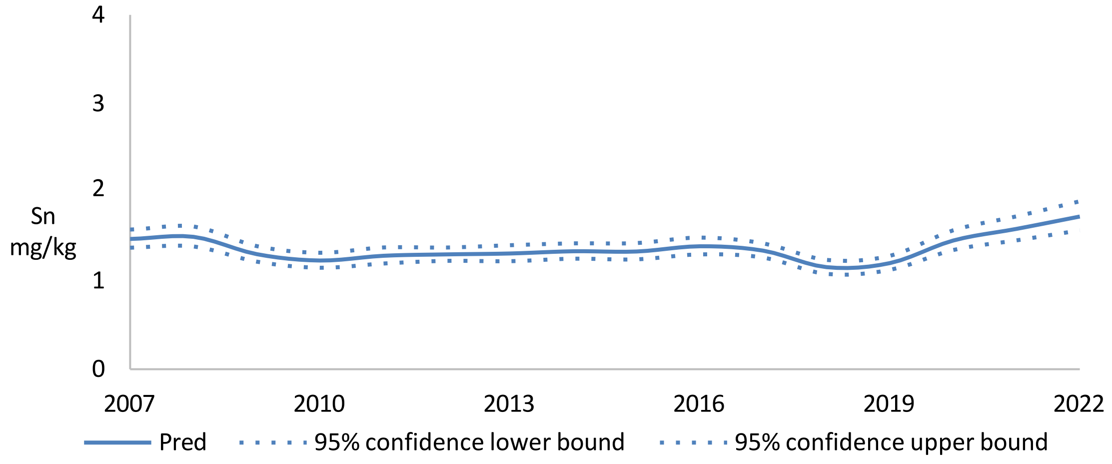

Figure 80. Change in mixed modelling average Sn concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

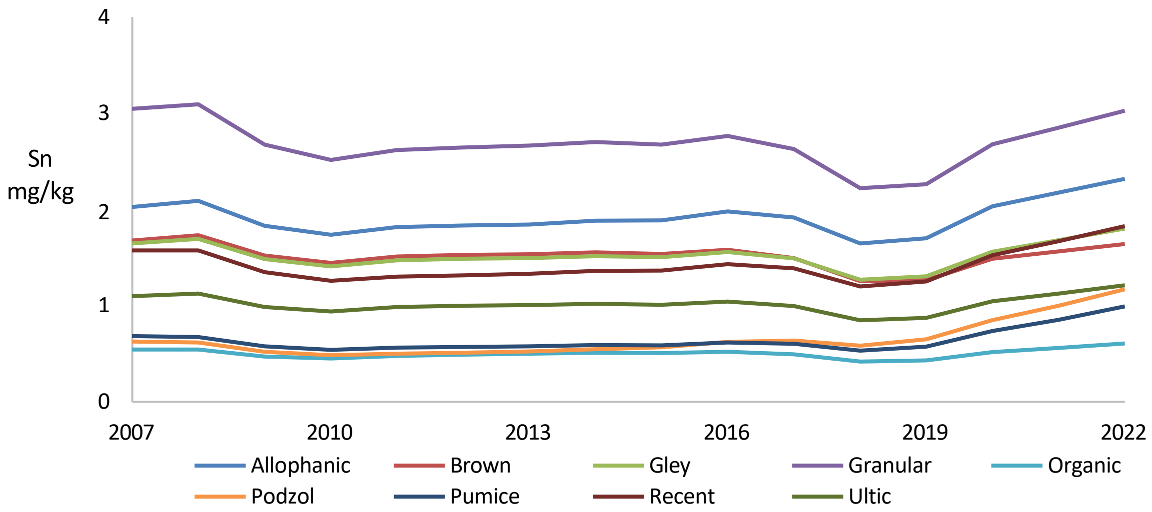

Figure 81. Change in mixed modelling average Sn 2007-2022 by soil order.

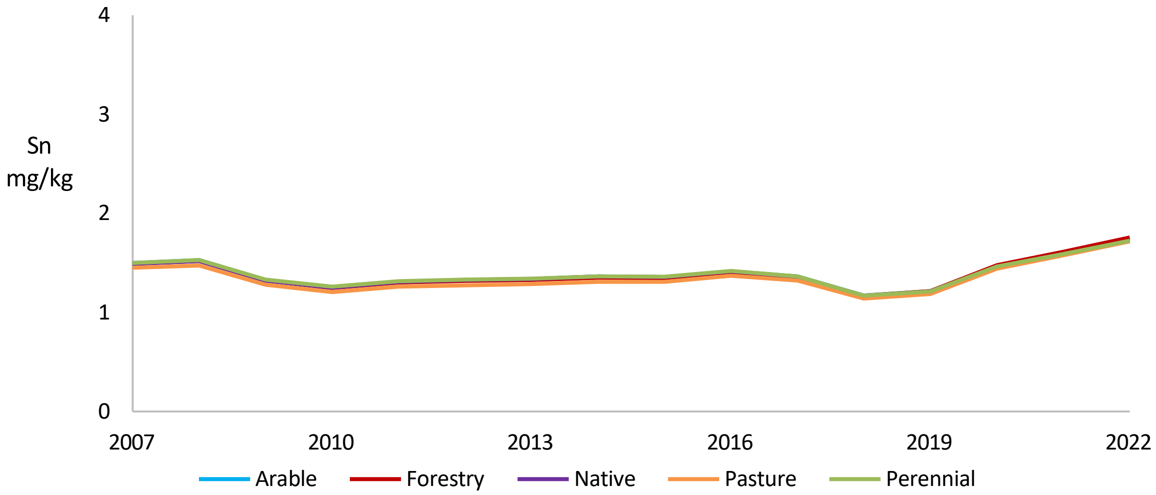

Figure 82. Change in mixed modelling average Sn 2007-2022 by land use.

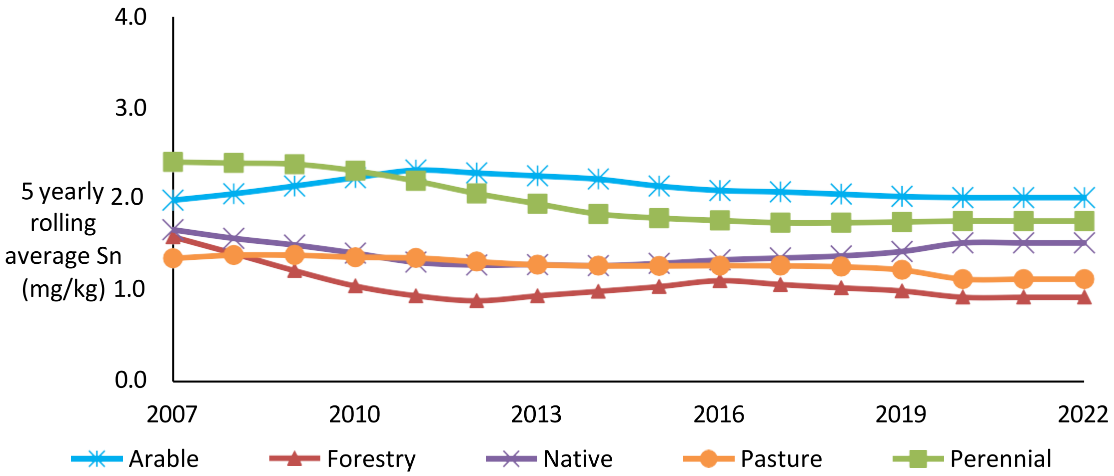

Figure 83. Average Sn by land use 2007-2022. Site Sn contents are well below the Netherlands intervention value for Sn (900 mg/kg, MIE 2009).

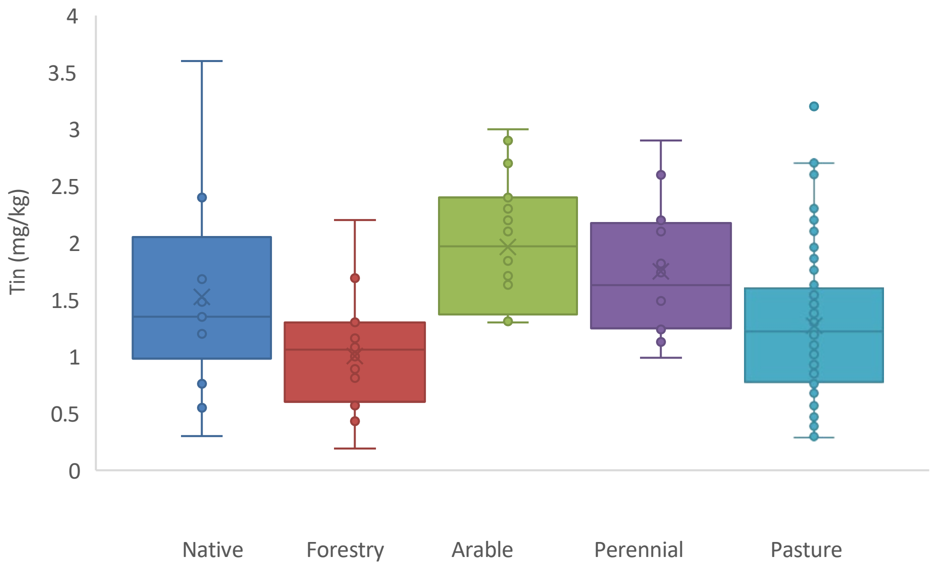

Figure 84. Boxpots of acid recoverable Sn (mg/kg) for most recent sampling up to 2022 for the five main land uses in the Waikato region

Uranium (U)

Uranium is found in all rocks, soil and water and is present in all phosphate rock used in the manufacture of phosphate fertilisers (Dupré de Boulois et al. 2008, Gavrilescu et al. 2009). It is not normally considered a priority trace element for human or environmental health, outside the nuclear industry, although the link with mineral P fertiliser is well established (Taylor 2007, 1997b, Rothbaum et al. 1979). Thus, guideline values for environmental management have come about due to studies associated with the nuclear industry. The United States Nuclear Regulatory Commission has established a residual contamination criterion for natural U in soil of 10 pCi/g, equivalent to 30 mg/kg (USNRC 1992), while the Canadian Council of Ministers of the Environment (2007) gave the final Soil Quality Guideline value for U for the protection of both human and environmental health as 23 mg/kg soil for agricultural land use. General chemistry principles suggest U should behave like As, but NZ has not established a soil guideline value for U for the protection of the environment or human health and the overseas guideline values discussed above were used.

Uranium is chemically noxious causing skin, lung, intestinal and bone marrow disorders, particularly where individuals have been chronically exposed by skin contact, ingestion or inhalation of dust, such as in phosphate mines and processing (Canu et al. 2012, 2011, Raymond-

Whish et al. 2007, Santos et al. 1995). In addition, U is a radioactive α emitter and exhibits genomic and other harmful effects (Busby & Schnug 2008).

There has significant accumulation of U in NZ soils under all fertilised land uses (Taylor 2016, 2007). Taylor & Kim (2008) showed U added to soil was initially in the more available soil fractions but added U became less available over time, with U relocated from the more available to the more resistant fractions of the soil. This can be attributed to the predominance in NZ of well oxidised, mildly acidic, highly organic soils, which have a strong affinity for U sorption. Very little U was soluble under these soil conditions with < 1% of the acid soluble fraction in soil solution (Taylor & Kim 2008). Therefore, in New Zealand, there was little risk of transfer of U from soil to other environmental domains, like water, or uptake into food. However, further applications of U contaminants in phosphate rock-based fertilisers were expected continue to accumulate in soil.

The mixed modelling results showed there was a non-significant nonlinear trend overall ($p>0.05$, Figure 85) and there were no significant ($p>0.05$) changes in trend or pattern for U by soil order (Figure 86) or land use (Figure 87). However, there were significant differences between land uses ($p<0.01$) and soil orders ($P<0.01$). Granular and Allophanic soils had higher average U concentrations than other soil orders, while Podzols, Pumice and Organic soils had the lowest average concentrations. Both mixed modelling and 5-yearly rolling average arable, perennial and pasture land uses had elevated levels of U compared to native, consistent with accumulation of U impurities from P fertilisers (Figures 14, 87-88). However, there is no clear statistically increasing trend for these land uses even though there appears to be slight increases in U concentrations in soils under arable and horticultural land uses. This lack of a clear trend is likely due to much lower applications of U than in the past. Historically, mineral P fertiliser used in NZ was derived from the ancient guano deposits, which contained relatively high U concentrations, about 60 mg/kg (Syers et al. 1986, Williams 1974, Menzel 1968, Trueman 1965). However, NZ currently buys its P rock on the world market and U concentrations measured more recently averaged 22.2 mg/kg (Taylor 1997).

No soil quality monitoring sites had U concentrations exceeding the guideline value for U for the protection of human and environmental health (23 mg/kg) in soil for agricultural land use (CCME 2007). However, chemical toxicity guideline values for U are lacking as current guideline values are based on radioactivity in Canada or the USA. Further information on the chemical ecotoxicity of U is desirable. Although no statistically significant trend was found, a watch should continue on U in the Waikato region due to its chemical and radioactive toxicity.

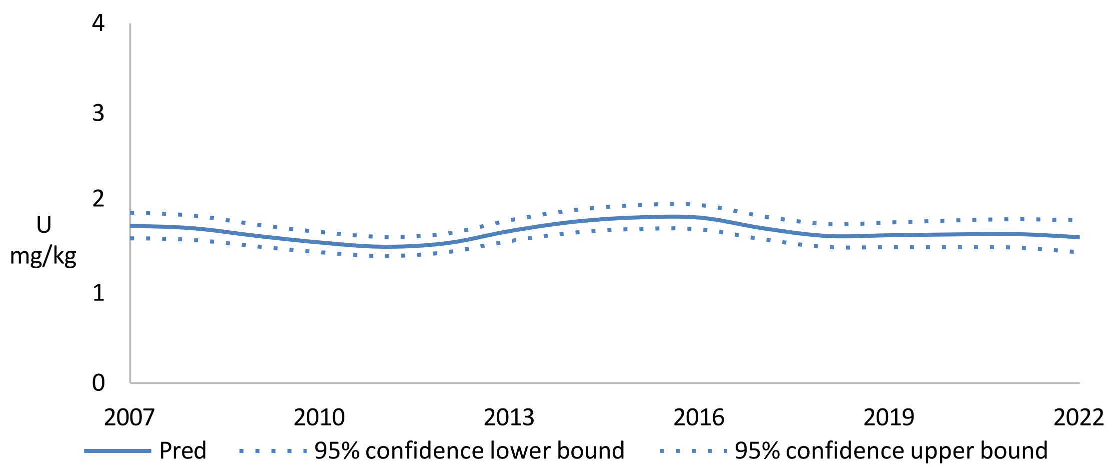

Figure 85. Change in mixed modelling average U concentration 2007-2022 for all sites (all land uses and soil orders) with 95% confidence limits.

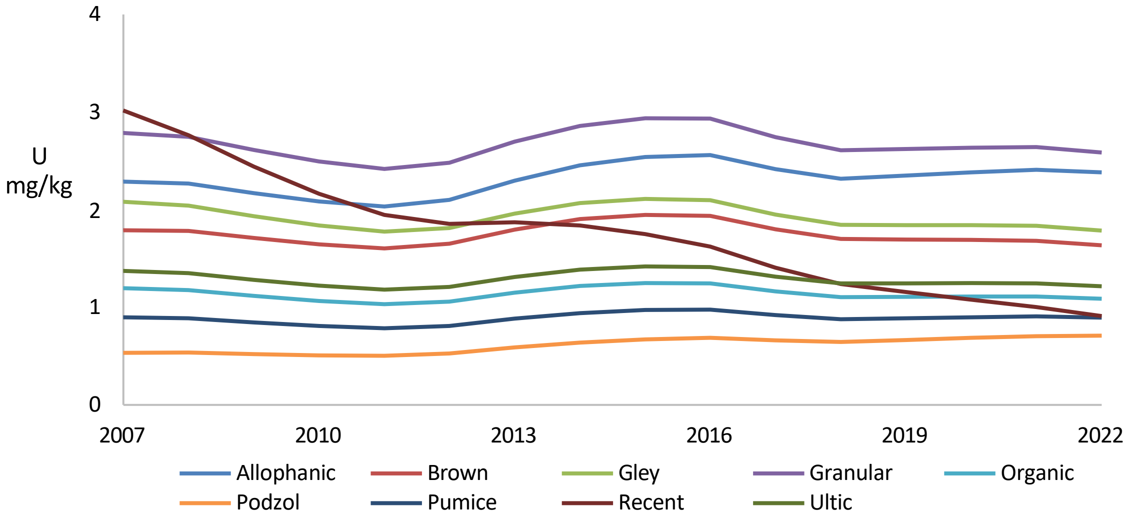

Figure 86. Change in mixed modelling average U 2007-2022 by soil order.

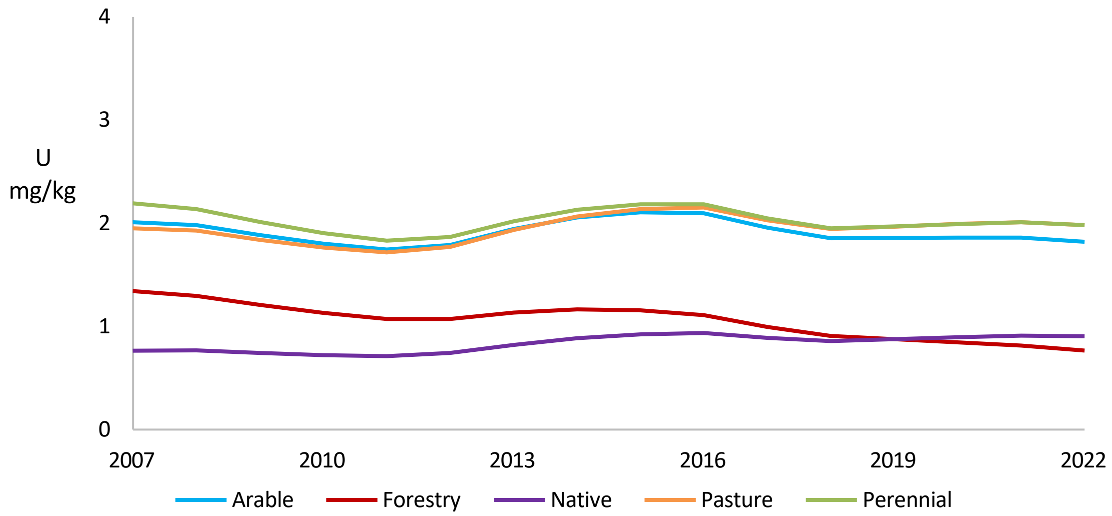

Figure 87. Change in mixed modelling average U 2007-2022 by land use.

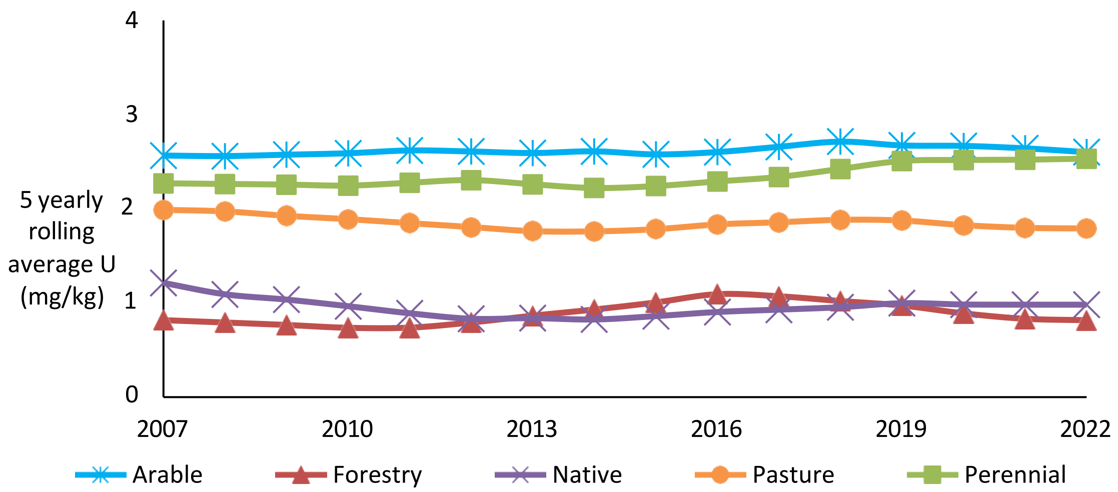

Figure 88. Average U by land use 2007-2022. Site U contents are below the Canadian Soil Quality Guideline value for the Protection of Environmental and Human Health of 23 mg/kg (CCME 2007).

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