A TRACE ELEMENT ANALYSIS OF SOIL QUALITY SAMPLES FROM THE WAIKATO REGION

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Abstract

Environment Waikato monitors 145 soil quality sites to determine the extent and direction of changes in soil condition. Sampling sites were chosen to cover a representative range of uses and Soil Orders including background and different farming systems. Samples were analysed for the trace elements arsenic, cadmium, chromium, copper, lead, mercury, nickel, uranium and zinc, to provide measures of defuse contamination. There were sufficient samples to assess data for 3 years but trends need to be considered indicative. Native and forestry sites had low concentrations of all trace elements measured, while other land uses showed enhancement of some elements. Annual cropping sites were significantly ($p<0.05$) enhanced in arsenic, cadmium, copper, chromium, lead, mercury, nickel, uranium and zinc. Horticultural sites were significantly enhanced ($p<0.05$) in arsenic, cadmium, copper, uranium and zinc, while dairy and other pasture sites were significantly enhanced ($p<0.05$) in cadmium, copper, uranium and zinc.

A separate land use category “conversion pasture” was developed to include a cluster of outliers that had been converted from production forestry to pasture. These sites have only been in pasture 2-3 years and still have trace element concentrations close to background. If these sites were included in the pasture categories, results were significantly skewed, e.g. a decrease in cadmium seen in soil under dairy pasture over the 3 years was due to the conversion of low-soil cadmium forestry sites to dairy, not to an actual decrease in soil cadmium under this land use.

Further monitoring over 2-3 years is required before a trend can be deemed genuine. Changes in land use are likely to lead to alterations in the trace element status of the soil.

Methods

Soil quality monitoring sites were chosen and sampled according to Land and Soil Monitoring: A guide for SoE and regional council reporting (Hill & Sparling 2009, Kim & Taylor 2009). Soils were classified according to the New Zealand Soil Classification (Hewitt et al 2003). Land use classes used were dairy (pasture grazed with milking cows), drystock (all other animal grazed pasture), arable (annual cultivation), horticulture (plants left in place), production forestry and background (native). A separate land use category “conversion pasture” was developed to include a cluster of outliers that had been converted from production forestry to pasture. These sites have only been in pasture 2-3 years and still have trace element concentrations close to background. If these sites were included in the pasture categories, results were significantly skewed, e.g. a decrease in cadmium seen in soil under dairy pasture over the 3 years was due to the conversion of low-soil cadmium forestry sites to dairy, not to an actual decrease in soil cadmium under this land use. There is only one year’s data for conversion pasture and indicative trends cannot be reported

Trace element analysis has been carried out on Waikato region soil quality sites since 2003 and it has only been within the last 3 years that sufficient data has been collected to make an initial assessment. All analyses were carried out at Hill Laboratories according to the Land and Soil Monitoring Manual (Kim & Taylor 2009). A subset of samples have been analysed twice, and/or at different laboratories, as a check on precision and accuracy of the results. In-house quality control standards and a standard reference river sediment (AGAL-10) were also analysed. All results are presented on a gravimetric basis.

Summary statistics were calculated using Data Desk version 6 and boxplots were produced using Sigma Plot version 7. The data was log-transformed to make a normal distribution for significance testing. Pooled Student's t-tests were used to assess significance of the difference between each pair of means.

Results are presented by land use class. These land uses include native, annual cropping (annual or more often cultivation), horticulture (crop stays in place every year), production forestry, dairy and other pastoral farming (e.g. deer, sheep, beef, cut and carry pasture).

Results

The effect of land use (Figure 1)

Native sites had low concentrations of all trace metals measured and were considered natural background. Forestry and conversion pasture sites also had low concentrations of all trace metals. The conversion pasture sites were recently converted from forestry and have received fertiliser and agricultural chemicals for only 2-3 years.

The other land uses measured were classes of land used for food production and have received fertiliser and agricultural chemicals for many years. Cadmium and uranium measurements were significantly ($p<0.05$) higher in soils under annual cropping, horticultural, dairy pasture and other pasture land uses than in soils under native and forestry consistent with the application contaminants in phosphate fertiliser.

Copper and zinc measurements were also significantly ($p<0.05$) higher in soils under annual cropping, horticultural, dairy pasture and other pasture land uses than in soils under native and forestry, consistent with the application of copper or zinc containing agricultural chemicals. There widespread distribution reflects the large number of products these 2 metals are used in.

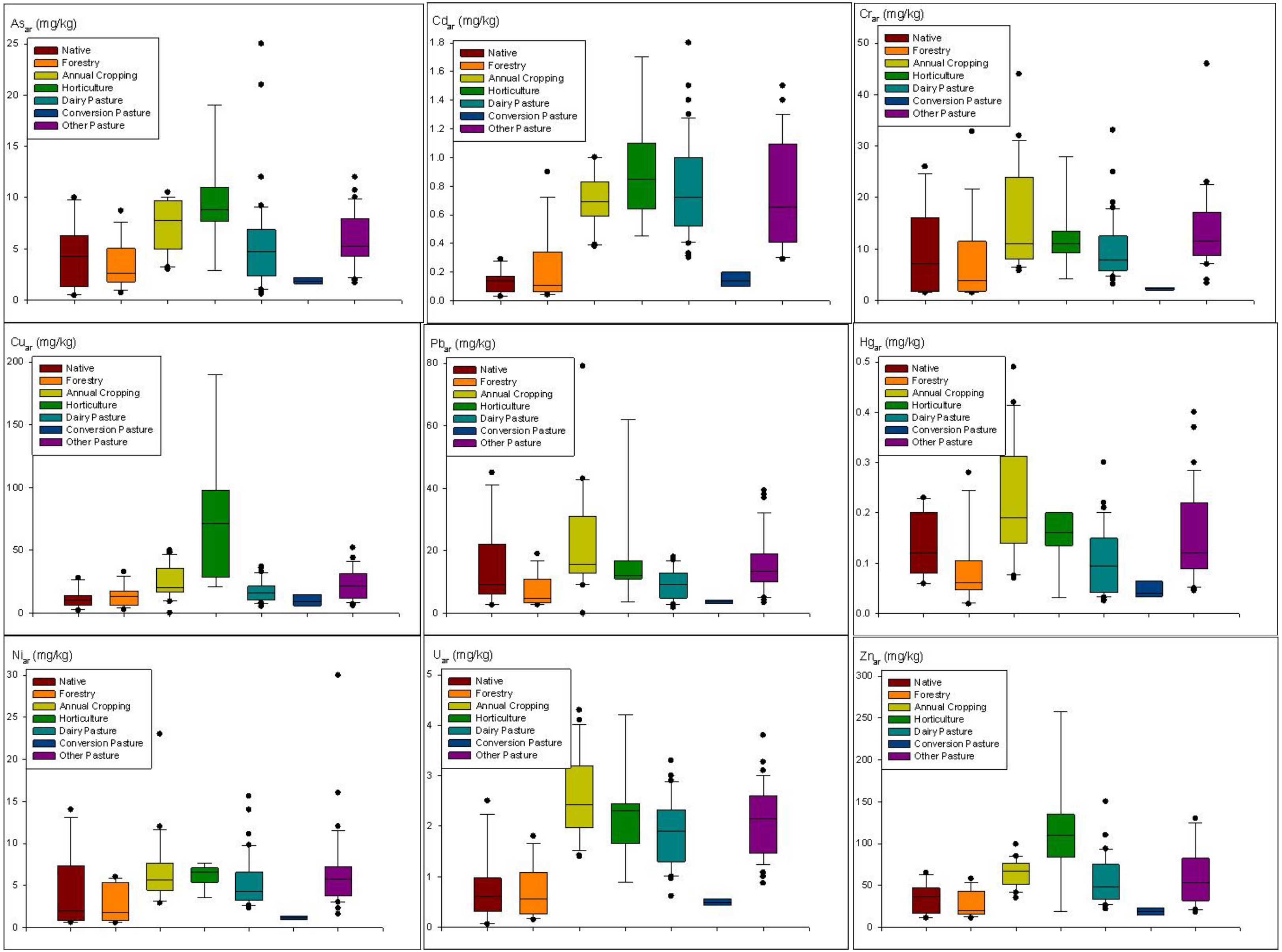
Arsenic measurements were significantly ($p<0.05$) higher in horticultural and annual cropping soils than in soils under other land uses, reflecting past use of arsenic containing pesticides.

Chromium, lead, mercury and nickel were significantly ($p<0.05$) higher in soils under annual cropping than in those under native and forestry. Horticultural, dairy pasture and other pasture land uses were also higher in nickel than native and forestry but these increases were not significant.

Discussion

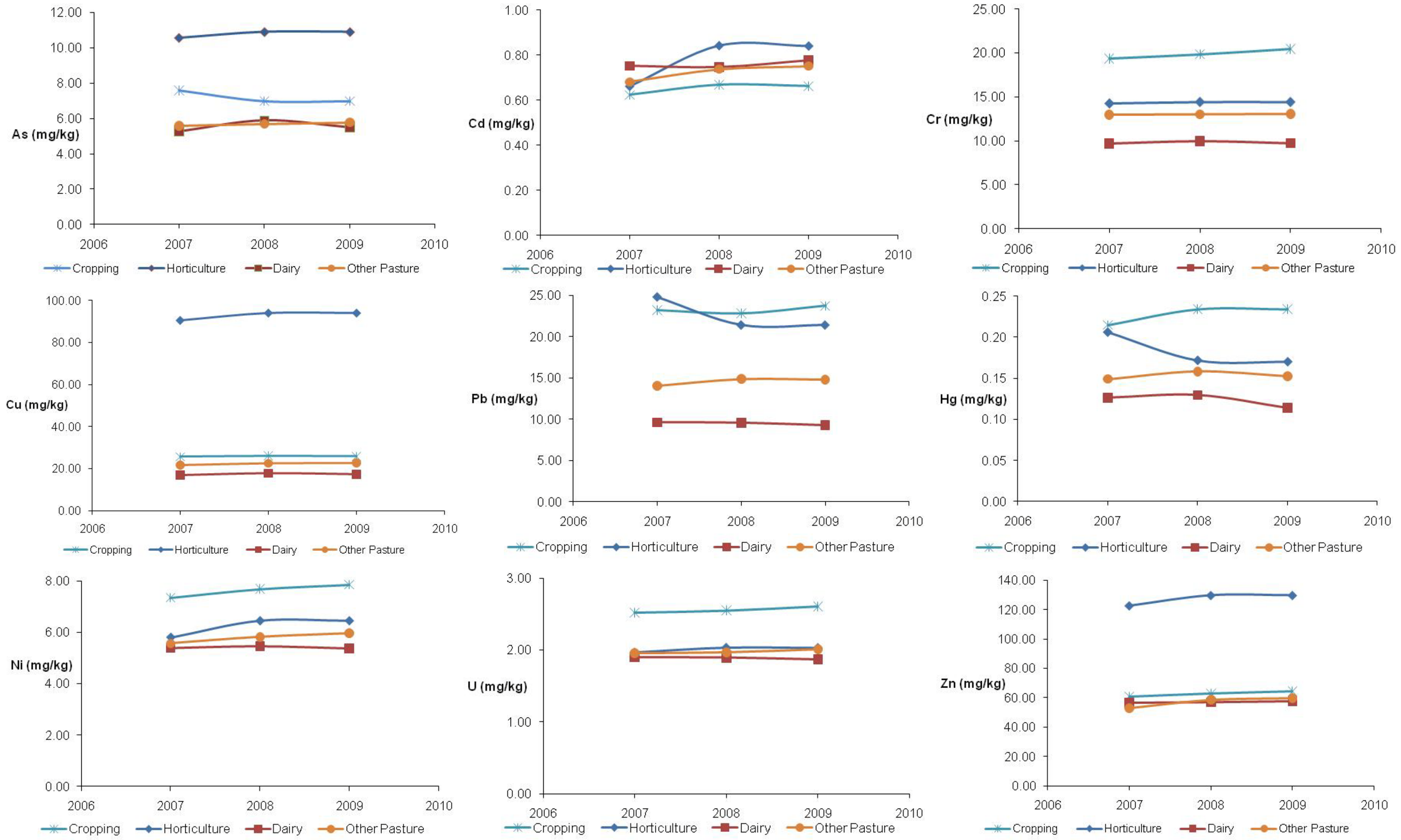
Native and forestry sites have low concentrations of all trace metals measured and did not show significant change, while there is only 1 years data for conversion pasture sites. Therefore, this discussion is limited to the 4 farmed land use classes. Elements fell into two groups, elements

Figure 1. The effect of land use on selected trace elements.



Middle line = median, box = upper and lower quarters, whiskers = 95% confidence interval.

Figure 2. Average values for selected trace elements in Waikato soils 2007-2009.



linked to use of phosphate fertilisers (cadmium and uranium), and elements linked to the use of agricultural chemicals used in farming (arsenic, chromium, copper, lead, mercury, nickel and zinc).

1. Elements associated with the use of phosphate fertiliser (cadmium and uranium)

Phosphate fertiliser is applies to cropping, horticulture, dairy and other pasture land uses, but little or no phosphate fertiliser is applied to forestry (sometimes after the third rotation of trees) and none (intentionally) to native. Phosphate fertiliser contains appreciable amounts of cadmium and uranium, as well as the minor element fluoride.

All cropping, (and native, forestry and conversion pasture) sites met the cadmium "tier 2" value (1 mg/kg) of the National Cadmium Management Strategy for New Zealand Agriculture (Cadmium Working Group 2011), while horticulture, dairy and other pasture had a proportion of sites exceeding this value (Table 1), and have higher soil cadmium (Figure 1). Cropping tends to use diammonium phosphate rather than superphosphate fertiliser, which is the predominate fertiliser used by the other land uses. Diammonium phosphate can have less cadmium content than superphosphate.

Cadmium is nationally recognised as an emerging issue for human and animal health, trade and ecology (Cadmium Working Group 2009) and historic accumulation rates of cadmium in Waikato soils were estimated to have averaged 0.006 mg cadmium /kg per year (Kim et al 2008). The average for the 4 farming land use classes is about 0.7mg/kg and the increase over the 3 year monitoring period is expected to be about 0.018 mg/kg or <3%. Annual cropping, dairy and other pasture concentrations increased by about the expected amount but this increase was not always consistent (Figure 2). Horticulture showed a large increase in 2008, part of which is explained by the addition to the data set of 2 new kiwifruit orchard sites with higher soil cadmium levels.

Table 1. Percent of soil quality sites meeting the cadmium "tier 2" value (CWG 2011).

	2009	**2008**	**2007**
Cropping	100	100	100
Horticulture	78	83	83
Forestry	100	100	100
Dairy	84	88	87
Other pasture	71	74	79

Another contaminant of phosphate fertiliser increasing in the region's soils is uranium. The highest uranium measurements were under annual cropping (Figure 1). It may be diammonium phosphate fertiliser contains more uranium than superphosphate. The natural background value for uranium in the Waikato region is 0.7 mg/kg (Figure 1), while cropping, horticulture and pastoral land uses are 2-3 times background. Uranium concentration consistently increased under annual cropping and other pastoral land uses (Figure 2), but there is a lack of information on what constitutes a safe concentration of uranium in the soil. Not only is uranium radioactive but it is also more chemically toxic than arsenic. In addition, uranium is important as it decays to radioactive daughter products including radon^{222} gas. Radon^{222} is considered a Group A human carcinogen by the World Health Organisation and the US Department of Health as it causes lung cancer and higher radon exposures cause more lung cancer. Radon^{222} is a significant public health problem in other parts of the world. All radon^{222} originates from uranium. Higher concentrations of uranium mean higher concentrations of radon^{222}. As suitable guidelines have yet to be developed, a watching brief only is kept on uranium by regional councils.

2. **Elements linked to the use of agricultural chemicals and treated timber used in farming (arsenic, copper, chromium, lead, mercury, nickel and zinc)**

The second group was elements linked to use of agricultural chemicals including animal remedies, veterinary medicines and pesticide use. Similar to the elements linked to the use of phosphate fertiliser, soils under cropping, horticulture, dairy and other pasture have much higher concentrations of elements linked to the use of agricultural chemicals and treated timber used in farming than those under forestry and native (Figure 1). Some of these elements, such as copper and zinc, are essential for growth but too much of them are toxic to life.

Concentrations of arsenic were significantly higher in horticultural and annual cropping soils than in soils under other land uses (Figure 1). There was extensive historic use of arsenic-containing insecticides, such as lead arsenate on horticultural and cropping land (Gaw et al 2006). Also, there have been instances within the Waikato region where developers have sort to convert orchards to residential land use, but soil arsenic concentrations exceeded both the recommended ceiling limit in agricultural soils (20 mg/kg) and the contaminated land investigation threshold (30 mg/kg) for arsenic under the new land use as a residential dwelling (Kim et al 2008). Historic and current use of CCA-treated timber in farming structures may also contribute arsenic to the soil. No clear trends were apparent over the 3 years (Figure 2). Further monitoring will confirm if the situation is constant.

Chromium, lead, mercury and nickel showed similar behaviour. They were significantly ($P<0.05$) higher in soils under annual cropping compared to those under other native and forestry (Figure 1) and this may be increasing (Figure 2). Historic use of the insecticide lead arsenate accounts for much of the lead enrichment observed on older horticultural soils. Historic and current use of CCA-treated timber in farming structures may also contribute chromium to the soil. Further monitoring over the next 2 years is needed to confirm this indicative trend.

Copper and zinc showed a wide range of values. Soil copper concentrations <5 mg/kg may result in copper deficiency in plants, while the figure is 10 mg/kg for zinc (Alloway 2008 a & b). Some sites under forestry (and native) land uses have soil copper below this level (Figure 1). The remoteness and difficulty in supplying copper fertiliser in the correct strength to these sites inhibits any foreseeable change. Copper is essential for animal growth and copper fertilisation or supplementation would be needed if these sites were converted to pasture. No sites had soil zinc below the 10 mg/kg figure (Figure 1). On the other hand, all farmed land uses showed enhanced soil copper and zinc. This result for farming type land uses is not unexpected given the wide spread use of copper and zinc agricultural-chemicals and CCA-treated wood. Copper may also be use as a livestock supplement. Widespread use of facial eczema remedies at annual zinc loadings of 5-7 kg/ha/y appears to have caused a significant increase in average zinc in Waikato pastoral soils from 28 mg/kg for background soil to 62 mg/kg for farmed soils (Taylor et al 2010). Assuming this accumulation has occurred over the last 25 years gives an estimated annual average accumulation rate of 1.36 mg Zn/kg/y. Zinc is also present in specific dithiocarbamate fungicides used in horticulture. Horticulture also had far higher levels of copper than other land uses (Figure 1) likely due to the use of copper fungicides. No clear trends are apparent (Figure 2). The decline in average soil copper for horticulture in 2009 was due to the inclusion of 2 organic kiwifruit orchards, low in soil copper, into the dataset.

A reminder: As data has been collected for a short time the discussion above should be considered indicative with confirmation coming over the next 2-3 years.

Conclusions

Sites under native and forestry land uses were not enhance in the trace elements measured. However, sites under all farming type land uses showed enhancement in some trace elements:

1. Annual cropping sites were significantly ($p<0.05$) enhanced in arsenic, cadmium, copper, chromium, lead, mercury, nickel, uranium and zinc
2. Horticultural sites were significantly enhanced ($p<0.05$) in arsenic, cadmium, copper, uranium and zinc
3. Dairy and other pasture sites were significantly enhanced ($p<0.05$) in cadmium, copper, uranium and zinc.

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