

## Concentrations of arsenic, cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage

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**Abstract** A national survey of agricultural topsoils and pastures was undertaken in the early 1990s to establish benchmark heavy metal concentrations. In total, 398 sites were sampled covering the major soil groups throughout the North and South Islands of New Zealand. Both pastoral farmed (312) and non-farmed (86) sites were sampled. Composite soil samples were taken from two depths, as well as pasture samples from the same area, and analysed for arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) concentrations. There was significant ( $P < 0.05$ ) enrichment of Cd at the 0–7.5 cm depth in five of the eight soil groups on farmed sites ( $0.44 \text{ mg kg}^{-1}$ ), over background non-farmed soils ( $0.20 \text{ mg kg}^{-1}$ ). Total soil Cd was highly correlated ( $P < 0.001$ ) to total soil phosphate (P) suggesting Cd enrichment in pastoral soils was related to fertiliser P applications. There was no enrichment of As, Cu, Pb, or Zn at the 0–7.5 cm depth on farmed soils compared with non-farmed soils. Results showed that soil concentrations of these elements were either typical of worldwide averages, or at the lower end of these ranges. There was, however, a significant ( $P < 0.05$ ) increase in Cu concentrations in the 0–2.5 cm depth on most farmed soils ( $14.3 \text{ mg kg}^{-1}$ ), compared with non-farmed

soils ( $11.4 \text{ mg kg}^{-1}$ ). The main difference in heavy metal concentrations between non-farm and pastoral pasture species was in the weed component. In general, the Cu, Zn, Pb, and As concentrations were essentially pedogenic in origin.

**Keywords** arsenic; cadmium; copper; zinc; lead; pastoral agriculture; soil groups; pasture species; grass; legume; weed; heavy metals; total phosphorus

### INTRODUCTION

Increased concern over the quality of the environment and the impact of human activities has focused attention on the pastoral agricultural practices that may be causing accumulation of heavy metals in the New Zealand environment. The amounts of heavy metals naturally present in soils are generally small. However, any contamination is serious because the contaminant or its breakdown products may eventually bioaccumulate in human food products.

Such accumulation of heavy metals in agricultural soils, over and above “native” levels, does occur (Rothbaum et al. 1979, 1986; Williams & David 1976) and has been related to the application of superphosphate fertiliser, at least in Australia and New Zealand. The heavy metals in phosphatic fertilisers are mainly derived from the original phosphate rock. Syers et al. (1986) measured the chemical composition of 10 phosphate rock materials and found concentrations ranging from 2–23  $\text{mg kg}^{-1}$  for arsenic (As), 3–100  $\text{mg kg}^{-1}$  for cadmium (Cd), 4–15  $\text{mg kg}^{-1}$  for copper (Cu), and 57–1010  $\text{mg kg}^{-1}$  for zinc (Zn). Lead (Pb) was not analysed, but concentrations ranging from 3 to 25  $\text{mg kg}^{-1}$  have been reported by other researchers (McLaughlin et al. 1996; van Kauwenbergh 1997). Concentrations of heavy metals in fertilisers vary depending on the source of rock and the ratio of acid to rock used in manufacture (Syers et al. 1986). In New Zealand, phosphatic fertilisers have been used

extensively either as superphosphate or via direct application of reactive phosphate rocks.

Heavy metals, such as Cd, accumulate in agricultural soils because they are not mobile (Bridges 1989). For example, in Australia 85% of the Cd applied in superphosphate over a 20-year period was shown to have remained in the cultivated layer (Williams & David 1976). While most heavy metals, except Cu and Zn, are not essential for plant growth or livestock health, plant uptake does occur. Plant uptake was found to be the significant point of entry of Cd into the food chain under sheep-grazed hill pastures (Roberts & Longhurst 2002). Soil ingestion by livestock may also represent another point of entry of heavy metals into the food-chain. Research in Britain and New Zealand has shown that cattle may ingest between 1 and 10% of dry matter intake in the form of soil, whereas sheep may ingest 30% or more, due to their closer grazing habit (Field & Purves 1964; Healy 1967, 1968, 1970; Thornton & Abrahams 1983).

Under pastoral farming conditions there are also other possible sources of heavy metals such as animal remedies. For example, anthelmintic drenches, injections, slow release rumen bullets, facial eczema treatments, and pluronics have potential for introducing heavy metals to animals.

This paper reports on results from a survey aimed at establishing benchmark concentrations of heavy metals in soils and pastures under New Zealand pastoral farming. The extent of heavy metal accumulation in the environment was also determined by comparing farmed sites with non-farmed sites across soil groups. Heavy metal enrichment is deemed to have occurred if pastoral soils have exceeded the "normal" (non-farmed) background concentrations and where this has occurred it is discussed in the text. Where possible international comparisons of concentrations have

been made, however much overseas soil data has been sampled at arable depths (between 0–10 and 0–20 cm). This paper is intended to serve as a useful reference for consultants and regional planners in dealing with resource consent and development issues.

## METHODS

### Survey approach

The survey was conducted on a total of 398 sites covering most of the major provinces in New Zealand. Both farmed pastoral and non-farmed sites were sampled. The non-farmed sites were areas of native bush, reserves, parks, or waste areas representative of the same soil groups sampled on the farmed sites.

In all, eight major soil groups were surveyed. Their New Zealand soil classification and soil taxonomy are given in Table 1 (Soil Survey Staff 1992; Hewitt 1998). These soils are referred to subsequently in this paper by their New Zealand genetic soil group classification (Taylor & Pohlen 1970), i.e., alluvial, brown granular loams (BGL), gleys, yellow-brown earths (YBE), yellow-brown loams (YBL), yellow-brown pumice (YBP), and yellow-grey earths (YGE), and organic (peat), respectively (Table 1).

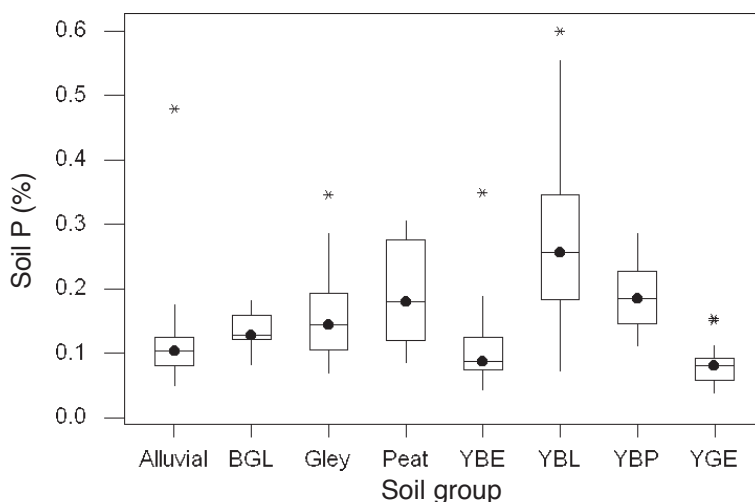
### Soil and pasture sampling

Composite soil samples (16 cores, 2.5 cm diameter) were taken at two depths, viz. 0–2.5 and 2.5–7.5 cm. This sampling regime was used as a means of increasing the ability to detect surface enrichment of small quantities of heavy metals. Soil data in this paper have also been integrated, to give a 0–7.5 cm depth estimate of heavy metal concentration, as this is the standard depth for pastoral soil fertility advice

**Table 1** Soil groups sampled and number of samples collected from non-farmed and farmed sites.

New Zealand genetic classification	Soil taxonomy		No. sites sampled	
	NZ	USA	Non-farmed	Farmed
Alluvial	Recent	Orthents	5	19
Brown granular loam	Granular	Humults	3	12
Gley	Gley	Aquepts/Aquepts	6	22
Peat	Organic	Fibrists/Sapristis	6	10
Yellow-brown earth	Ultic	Aquults	24	82
Yellow-brown loam	Allophanic	Cryands/Udlands	23	72
Yellow-brown pumice	Pumice	Vitrands/Vitricyands	6	22
Yellow-grey earth	Pallic	Hapludalfs	13	73

**Fig. 1** Total P (%) at 0–7.5 cm depth for farmed sites by soil groups. Median values = bar in the middle of the box; the top and bottom of the box = 25–75% interquartile range; whiskers = non-outlier minimum and maximum; asterisk = extreme outlier values.



in New Zealand, and unless stated otherwise the following results refer to the integrated 0–7.5 cm depth.

Pasture samples were also collected from the same area as the soil samples. These pasture samples were later dissected into their grass, legume, and weed components. On four occasions in North Canterbury/Marlborough region, experiencing drought conditions, the pasture species collected consisted of a single genus, e.g., lucerne (*Medicago sativa*), as an alternative to desiccated pasture.

### Analytical techniques

#### Soils

All soil samples were air-dried at 35°C, ground in a Teflon-coated ceramic mortar, and sieved to pass a 75- $\mu$ m mesh before analysis. Soil samples (0.5 g) were digested with a mixture of concentrated perchloric (70%) (2 ml) and nitric acid (5 ml) before dilution and total element determination. Cadmium and Pb digests were diluted to 25 ml with distilled water (2% perchloric matrix) before measuring concentrations by graphite furnace atomic absorption spectrophotometry (GFAAS). Copper and zinc digests were diluted to 10 ml (20% perchloric matrix) and concentrations determined by flame AAS (FAAS). Arsenic was determined by hydride generation technique. Sodium borohydride (2 ml) was injected into tubes containing digested material in the concentrated perchloric matrix (2 ml) and mixed with 1 ml 50% hydrochloric acid/water before concentrations were determined by AAS using a heated quartz cell. Total P was measured in the above acid extracts, suitably diluted, by inductively coupled

plasma emission (ICP). All soil results are expressed on a dry-weight basis. Limits of detection (LOD) ( $\text{mg kg}^{-1}$ ) were 0.01 for Cd and As; 0.1 for Pb; and 1.0 for Cu and Zn.

#### Herbage

All plant samples were washed in cold water and oven-dried at 60°C then ground to pass a 2-mm mesh sieve. Herbage (1 g) was digested using the same nitric/perchloric acid procedure described above for the soils and diluted to 25 ml. Concentrations of Cd and Pb were determined by GFAAS, Zn and Cu by FAAS and As by AAS. LOD ( $\text{mg kg}^{-1}$ ) for As and Cd: 0.01; Pb: 0.1; and Cu and Zn: 1.0. All herbage results are reported on a dry-weight basis.

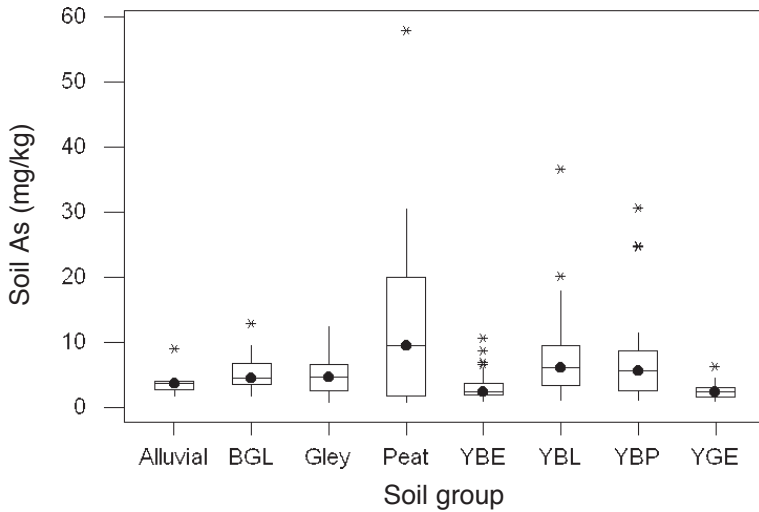
#### Statistical procedure

The data were analysed using standard (unbalanced) analysis of variance (ANOVA) techniques. All variables were log-transformed prior to analysis. Soil data are presented as box and whisker figures showing median and interquartile ranges (IQR). Pasture results are reported in tables as median values. The ANOVA results are discussed in the text and where appropriate the minimum significant ratio (MSR) reported.

## RESULTS AND DISCUSSION

### Soil groups

The number of samples collected across the various soil groups for both non-farmed and farmed sites are given in Table 1. In total, 86 non-farmed sites and 312 farmed sites were sampled.



**Fig. 2** Soil arsenic (As) concentrations (mg kg<sup>-1</sup>) at 0–7.5 cm depth for farmed pastoral sites by soil groups. Key as for Fig. 1.

**Soil concentrations**

*Total P*

Median total P concentrations (%) on farmed soils were: alluvial (0.10), BGL (0.13), gley (0.14), peat (0.18), YBE (0.09), YBL (0.25), YBP (0.19), and YGE (0.08) (Fig. 1). Soil total P was significantly higher ( $P < 0.05$ ) on pastoral soils compared with their corresponding non-farmed soils for BGL, gley, YBL, YBE, and YBP soil groups. These higher total P contents for pastoral soils are consistent with the use of phosphatic fertilisers to enhance pasture productivity, and the differences in concentration reflected the degree of fertiliser P input. While there was a highly significant correlation ( $P < 0.001$ ) between total P and total Cd enrichment of pastoral soils (Roberts et al. 1994), the relationships between total P and the other heavy metals were generally not significant.

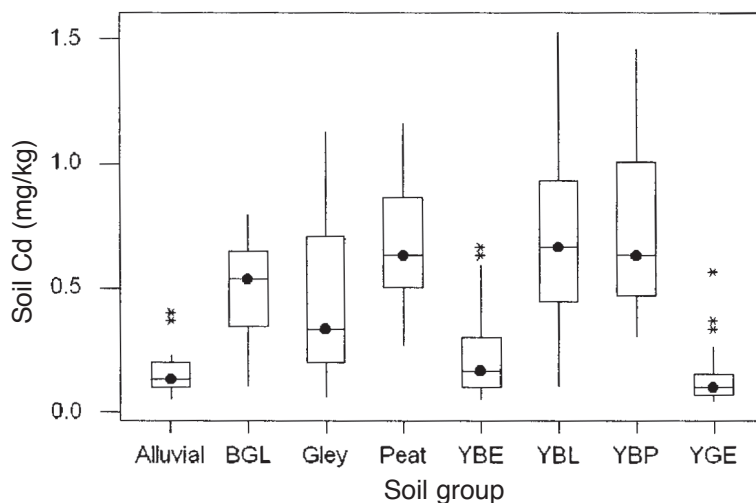
*Arsenic*

*Soil As:* Median As concentrations for 0–7.5 cm depth for farmed soils are presented in Fig. 2. The median As concentrations across the soil groups ranged from lowest for YGE soils (2.3 mg kg<sup>-1</sup>) to highest in peats (9.5 mg kg<sup>-1</sup>). Peat soils also had the highest As concentrations for non-farmed sites, but the enrichment above pastoral levels was not significant. However, there was significant ( $P < 0.05$ ) enrichment of As at both 0–2.5 and 2.5–7.5 cm depths on farmed YBL soils compared with non-farmed soils; these values were 5.9 mg kg<sup>-1</sup> versus 3.2 mg kg<sup>-1</sup> for the 0–7.5 cm depth, respectively. There was little difference in As concentrations between farmed and non-farmed sites for the other soil groups. Arsenic concentrations on farmed soils were higher (5.4 mg kg<sup>-1</sup>) at the 2.5–7.5 cm depth compared with the 0–2.5 cm depth (3.9 mg kg<sup>-1</sup>).

**Table 2** Median and interquartile ranges of arsenic concentrations (mg kg<sup>-1</sup>) in herbage on farmed soils.

	Alluvial	BGL	Gley	Peat	YBE	YBL	YBP	YGE
<i>Grass</i>								
Median	0.09	0.12	0.14	0.24	0.07	0.10	0.09	0.10
IQR	0.06–0.14	0.05–0.19	0.05–0.17	0.10–0.25	0.05–0.12	0.05–0.19	0.06–0.17	0.06–0.14
<i>Legume</i>								
Median	0.11	0.13	0.08	0.10	0.11	0.08	0.07	0.11
IQR	0.07–0.18	0.11–0.14	0.05–0.10	0.05–0.15	0.06–0.15	0.05–0.14	0.04–0.09	0.08–0.14
<i>Weed</i>								
Median	0.10	0.08	0.07	0.09	0.11	0.07	0.11	0.10
IQR	0.07–0.11	0.06–0.11	0.05–0.10	0.06–0.17	0.06–0.18	0.04–0.12	0.05–0.18	0.06–0.15

**Fig. 3** Soil cadmium (Cd) concentrations ( $\text{mg kg}^{-1}$ ) at 0–7.5 cm depth for farmed pastoral sites by soil groups. Key as for Fig. 1.



The As concentrations found were similar to the mean background levels of  $4.5 \text{ mg kg}^{-1}$  (range 0.02–24) for the 0–15 cm depth found at 99 sites in the Auckland region (Auckland Regional Council 1999). Kabata-Pendias & Pendias (1992) reported the As content of surface soils worldwide as ranging from  $<1$  to  $95 \text{ mg kg}^{-1}$ , however concentrations in most soil groups are normally below  $10 \text{ mg kg}^{-1}$ . It would appear that soil As concentrations of farmed soils in New Zealand are at the lower end of the worldwide range.

**Pasture As:** The median As concentrations in pasture species are presented in Table 2. Highest As concentrations were found on peat soils in non-farm grasses (median:  $0.34 \text{ mg kg}^{-1}$ , IQR: 0.27–0.41) which was significantly ( $P < 0.05$ ) higher than for pastoral grasses. Conversely, non-farm legumes on peat soils had significantly lower median concentrations ( $0.04 \text{ mg kg}^{-1}$ ) than pastoral legumes ( $0.10 \text{ mg kg}^{-1}$ ). Significantly higher As concentrations ( $P < 0.05$ ) were found in pastoral

weeds on YBE and YGE soils compared with their non-farmed sites.

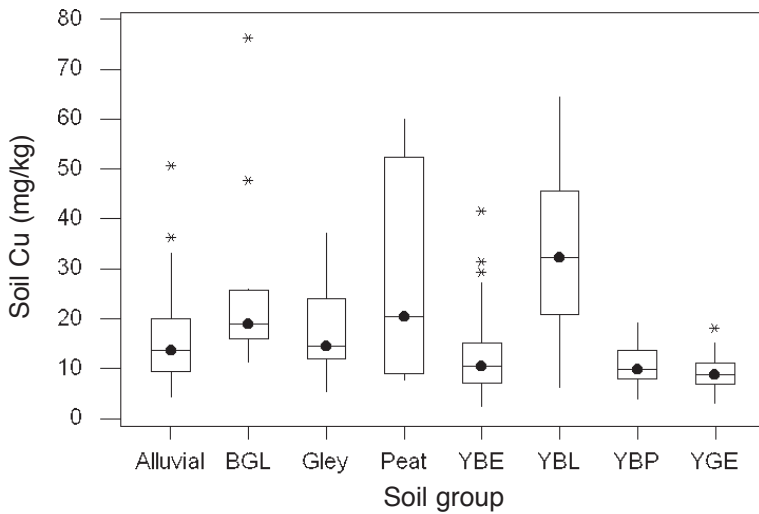
Most other studies on As have been related to contaminated sites or release into the environment from geothermal sources. Aggett & Aspell (1980) reported concentrations of  $0.42$  and  $0.38 \text{ mg kg}^{-1}$  for ryegrass (*Lolium perenne*), and white clover (*Trifolium repens*), respectively.

#### Cadmium

**Soil Cd:** Cadmium enrichment occurred on farmed soils ( $0.44 \text{ mg kg}^{-1}$ ), relative to non-farmed soils ( $0.20 \text{ mg kg}^{-1}$ ), except for YGE, and this was significant ( $P < 0.05$ ) for BGL, Gley, Peat, YBL, and YBP soil groups as previously reported (Roberts et al. 1994). The median Cd concentrations in farmed soils were lowest on YGE soils ( $0.10 \text{ mg kg}^{-1}$ ) and highest for YBL soils ( $0.67 \text{ mg kg}^{-1}$ ) (Fig. 3) reflecting median Total P values (0.08 and 0.26%, respectively). Roberts et al. (1994) reported that soil Cd was highly correlated ( $P < 0.001$ ) with soil Total

**Table 3** Median and interquartile ranges of cadmium concentrations ( $\text{mg kg}^{-1}$ ) in herbage on farmed soils.

	Alluvial	BGL	Gley	Peat	YBE	YBL	YBP	YGE
<i>Grass</i>								
Median	0.06	0.05	0.05	0.06	0.08	0.06	0.18	0.08
IQR	0.04–0.10	0.04–0.06	0.04–0.08	0.04–0.14	0.05–0.15	0.04–0.11	0.08–0.31	0.05–0.10
<i>Legume</i>								
Median	0.03	0.04	0.05	0.04	0.05	0.03	0.06	0.05
IQR	0.02–0.06	0.04–0.04	0.03–0.06	0.03–0.05	0.04–0.11	0.02–0.06	0.05–0.09	0.03–0.08
<i>Weed</i>								
Median	0.19	0.29	0.18	0.20	0.18	0.21	0.23	0.19
IQR	0.12–0.26	0.15–0.50	0.09–0.47	0.15–0.48	0.12–0.31	0.11–0.35	0.18–0.30	0.12–0.28



**Fig. 4** Soil copper (Cu) concentrations ( $\text{mg kg}^{-1}$ ) at 0–7.5 cm depth for farmed pastoral sites by soil groups. Key as for Fig. 1.

P, and suggested that Cd enrichment in pastoral soils was related to phosphatic fertiliser use.

**Pasture Cd:** Median Cd concentrations in grasses on farmed sites (Table 3) ranged from 0.05 to 0.18  $\text{mg kg}^{-1}$  across soil groups, compared with 0.04–0.10  $\text{mg kg}^{-1}$  for non-farmed soils. Cadmium content of grasses was significantly correlated ( $P < 0.05$ ) with soil Cd (0–7.5 cm) (Roberts et al. 1994). Cadmium content in grasses ranged from 0.03 to 0.30  $\text{mg kg}^{-1}$  reflecting species differences. Even within grass cultivars Cd content can range considerably, e.g., in ryegrass cultivars, pasture Cd concentrations averaged 0.05  $\text{mg kg}^{-1}$ , but ranged between 0.03 and 0.12  $\text{mg kg}^{-1}$  (Roberts & Longhurst unpubl. data).

Median Cd concentrations in legumes were lower than in grasses, ranging from 0.03 to 0.06  $\text{mg kg}^{-1}$  for farms across the soil groups (Table 3) compared with 0.03–0.10  $\text{mg kg}^{-1}$  for legumes on non-farmed soils. Within legume species, white clover dominated pastoral sites and had lower Cd concentrations than lotus species (*Lotus pedunculatus*)

which was usually the only legume present on non-farmed sites. Weed Cd content ranged from medians of 0.19–0.23  $\text{mg kg}^{-1}$  in a relatively uniform distribution across the farmed soil groups (Table 3) compared with 0.07–0.19  $\text{mg kg}^{-1}$  for non-farmed soils. Roberts et al. (1994) reported that weed Cd was significantly correlated ( $P < 0.05$ ) with soil Cd (0–7.5 cm).

**Copper**

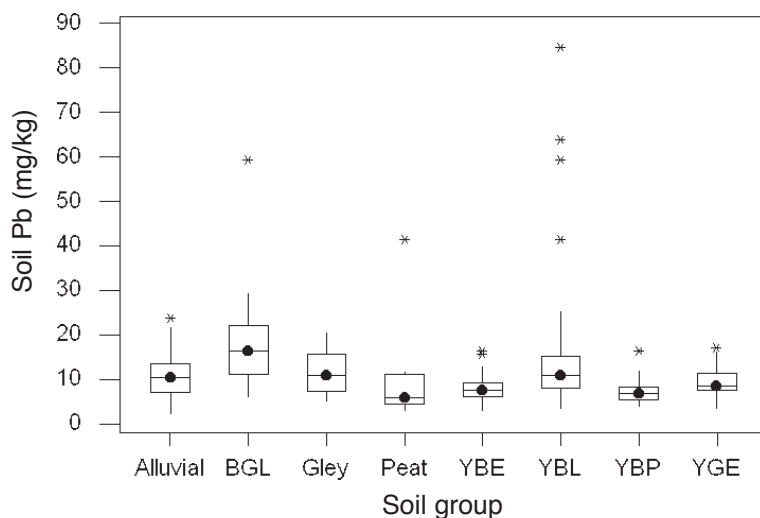
**Soil Cu:** Median soil Cu concentrations were lowest in YGE soils (8.7  $\text{mg kg}^{-1}$ ) and highest in YBL soils (32.3  $\text{mg kg}^{-1}$ ) (Fig. 4). Copper concentrations at 0–7.5 cm depth on farmed soils were not significantly higher than those on non-farmed soils, however there was a significant ( $P < 0.05$ ) enrichment of Cu in the top 2.5 cm of all farmed soils, except the YBE, compared with non-farmed soils (14.3  $\text{mg kg}^{-1}$  versus 11.4  $\text{mg kg}^{-1}$ , respectively, MSR: 1.2).

The Cu values found in this survey were similar to the mean concentration of 17.5  $\text{mg kg}^{-1}$  in New

**Table 4** Median and interquartile ranges of copper concentrations ( $\text{mg kg}^{-1}$ ) in herbage on farmed soils.

	Alluvial	BGL	Gley	Peat	YBE	YBL	YBP	YGE
<i>Grass</i>								
Median	11	11	10.5	10	11	10	9	9
IQR	10–12.5	11–11	8–12	9–11.3	9–13	9–11	8–9	8–11
<i>Legume</i>								
Median	12	11	11	11	12	11.5	10.5	13
IQR	8.5–13	10–14	8.5–13	10–14.3	10–15	10–13	8–13	10–16
<i>Weed</i>								
Median	11	11	10	14.5	13	12.5	10.5	15
IQR	8–14.3	9–13.8	8.3–12.5	11.5–15.5	10.3–15.8	10.5–14.5	8–12	12–18

**Fig. 5** Soil lead (Pb) concentrations ( $\text{mg kg}^{-1}$ ) at 0–7.5 cm depth for farmed pastoral sites by soil groups. Key as for Fig. 1.



Zealand pastoral soils reported by Wells (1957). However, a recent survey by the Auckland Regional Council (1999) reported higher mean concentrations of  $27 \text{ mg kg}^{-1}$  (range 1–111) for the 0–15 cm depth in their area. The average total Cu content in 7819 uncontaminated soil samples from various parts of the world was  $26 \text{ mg kg}^{-1}$  (range 2–100) (Ure & Berrow 1982). Attempting to exclude contaminated sites, Kabata-Pendias & Pendias (1992) reported total Cu content of uncontaminated surface soils worldwide as varying from 13 to  $24 \text{ mg kg}^{-1}$ .

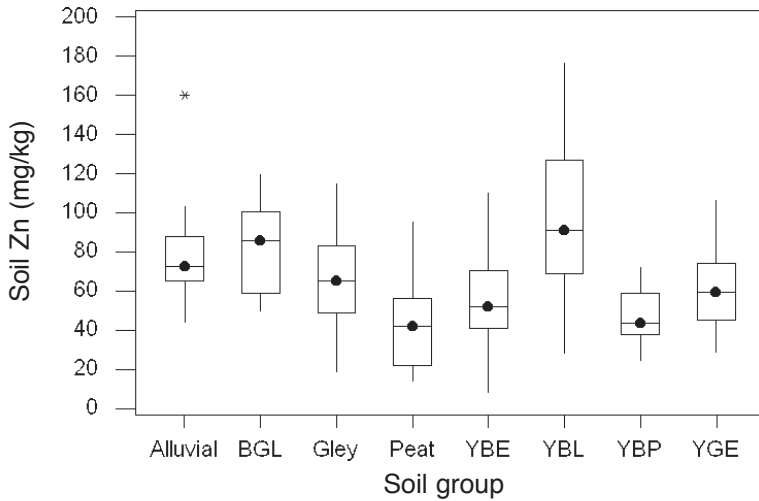
While there has been enrichment of Cu in the top 2.5 cm layer of pastoral soils in New Zealand, soil concentrations appear to be typical of those found worldwide. It is possible that agricultural practices such as applying copper sulphate in fertilisers (typically at  $5 \text{ kg Cu ha}^{-1}$ ), injecting or administering intraruminally slow-release Cu needles or boluses to grazing animals and their subsequent excretion may be contributing to this accumulation.

*Pasture Cu:* The median Cu concentrations in farmed pasture species were highest on YGE soils and lowest on YBP soils (Table 4). Wells (1957) also found the lowest Cu concentrations in sweet vernal grass (*Anthoxanthum odoratum*) when grown on YBP soils derived from rhyolitic ash. The weed species tended to have higher Cu concentrations (not significant) than grasses or legumes, but the Cu content in weeds was significantly higher ( $P < 0.05$ ) on non-farmed soils ( $13.5 \text{ mg kg}^{-1}$ ) than on farmed soils ( $11.9 \text{ mg kg}^{-1}$ ). The mean values found in this survey were similar to those found by Metson et al. (1979) who monitored Cu every month for 1 year at seven sites in the lower North Island and found mean concentrations of  $10.5 \text{ mg kg}^{-1}$  (range 7.7–13.5) and  $12.0 \text{ mg kg}^{-1}$  (range 8.1–17.6) for grass and clovers, respectively.

Copper is essential for both plant nutrition and animal health, and pasture concentrations of  $10 \text{ mg kg}^{-1}$  or greater are considered adequate for New

**Table 5** Median and interquartile ranges of lead concentrations ( $\text{mg kg}^{-1}$ ) in herbage on farmed soils.

	Alluvial	BGL	Gley	Peat	YBE	YBL	YBP	YGE
<i>Grass</i>								
Median	0.25	0.35	0.30	0.10	0.20	0.20	0.20	0.30
IQR	0.20–0.40	0.30–0.40	0.20–0.40	0.10–0.32	0.20–0.30	0.10–0.30	0.10–0.30	0.20–0.40
<i>Legume</i>								
Median	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
IQR	0.10–0.30	0.10–0.20	0.10–0.10	0.10–0.15	0.10–0.10	0.10–0.20	0.10–0.10	0.10–0.10
<i>Weed</i>								
Median	0.10	0.10	0.10	0.10	0.10	0.10	0.30	0.10
IQR	0.10–0.12	0.10–0.60	0.10–0.27	0.10–0.65	0.10–0.25	0.10–0.40	0.10–0.40	0.10–0.25



**Fig. 6** Soil zinc (Zn) concentrations (mg kg<sup>-1</sup>) at 0–7.5 cm depth for farmed pastoral sites by soil groups. Key as for Fig. 1.

Zealand conditions (Morton et al. 1999). Copper concentrations in this survey were below 10 mg kg<sup>-1</sup> on 10% of the pastoral sites.

*Lead*

*Soil Pb:* The median concentrations for Pb on farmed soils are shown in Fig. 5. Lead concentrations were lowest on peat soils (6 mg kg<sup>-1</sup>) and highest on BGL soils (16 mg kg<sup>-1</sup>). Overall, there was no significant difference in Pb concentrations between depths in farmed soils, and while there were differences in Pb concentration within soil groups on pastoral sites, these were not significantly different from the non-farmed sites.

Aubert & Pinta (1977) reported that soils are often richer in Pb than the parent rocks from which they are derived and average 15–25 mg kg<sup>-1</sup>. Ure & Berrow (1982) calculated an average concentration of 29 mg kg<sup>-1</sup> from 4970 soils worldwide, while Kabata-Pendias & Pendias (1992) reported a

worldwide mean Pb concentration of 32 mg kg<sup>-1</sup> (range 10–67 mg kg<sup>-1</sup>). Lead concentrations in New Zealand pastoral soils are clearly at the lower end of these worldwide ranges.

*Pasture Pb:* The median Pb concentrations in pasture species are presented in Table 5. The highest median Pb concentrations were found in the non-farm weeds on BGL and gley soils (1.0 mg kg<sup>-1</sup>). Lead concentrations were significantly higher (*P* < 0.05) in non-farmed legumes (0.29 mg kg<sup>-1</sup>) and weeds (0.51 mg kg<sup>-1</sup>) compared with pastoral sites (0.21 and 0.26 mg kg<sup>-1</sup>, respectively). The difference in Pb concentrations in legumes is most likely due to lotus, the dominant legume species on non-farmed sites, accumulating more Pb (0.10–0.36 mg kg<sup>-1</sup>) than pastoral clovers (0.11–0.16 mg kg<sup>-1</sup>).

Little data are available on “normal” pasture concentrations in New Zealand. Overseas, Mitchell & Reith (1966) reported that typical Pb concentrations in mixed pastures range from 0.3 to

**Table 6** Median and interquartile ranges of zinc concentrations (mg kg<sup>-1</sup>) in herbage on farmed soils.

	Alluvial	BGL	Gley	Peat	YBE	YBL	YBP	YGE
<i>Grass</i>								
Median	92	74	65	71	84	70	71	96
IQR	56–110	61–82	51–86	64–99	58–106	56–98	61–82	70–152
<i>Legume</i>								
Median	92	88	76	79	95	98	80	106
IQR	72–153	71–120	65–88	68–92	72–124	72–130	67–121	68–156
<i>Weed</i>								
Median	117	65	81	108	140	99	65	172
IQR	84–139	54–146	67–116	67–156	89–187	70–129	59–107	118–233

1.5 mg kg<sup>-1</sup> during periods of active growth. However, they also reported that a variation of up to 100-fold in the Pb content can occur in pasture at different stages of growth, and that this variation was the largest of the 25 elements analysed. Kabata-Pendias & Pendias (1992) reported mean Pb levels and ranges in grasses and legumes at immature growth stages from different countries as 2.3 mg kg<sup>-1</sup> (0.19–15.0) and 3.8 (1–18.8), respectively. Lead concentrations under New Zealand pastoral farming conditions indicate levels at the lower end of worldwide concentrations.

### Zinc

*Soil Zn:* The median total Zn concentrations for farmed soils show that highest values were found on YBL soils (91 mg kg<sup>-1</sup>) with lowest values on peat soils (42 mg kg<sup>-1</sup>) (Fig. 6). These results support earlier findings by Whitton & Wells (1974) who reported mean Zn concentrations of 104 mg kg<sup>-1</sup> (range 51–177) and 27 mg kg<sup>-1</sup> (range 21–34) for YBL and organic (peat) soils, respectively. The farmed volcanic soils (YBL and BGL) had significantly higher ( $P < 0.05$ ) Zn concentrations than their non-farmed soils due to enrichment in the top 2.5 cm depth.

The overall mean total Zn content of 60 mg kg<sup>-1</sup> was reported for 7402 worldwide soils (Ure & Berrow 1982), while Kabata-Pendias & Pendias (1992) reported a worldwide mean of 64 mg kg<sup>-1</sup> (range 17–125 mg kg<sup>-1</sup>). Zinc concentrations in New Zealand soils appear to be similar to average worldwide concentrations. Unlike Cd, there appears to be no systemic accumulation of Zn in pastoral soils compared with non-farmed soils (Roberts et al. 1994). The greater natural abundance of Zn in soils makes the detection of exogenous additions of Zn to soils more difficult.

*Plant Zn:* Median Zn concentrations in pasture species are presented in Table 6 and show that the highest values are found in weed species particularly on YBE and YGE soils. Median Zn values appear to vary widely between pasture species, soil groups, and farmed or non-farmed sites. Lowest Zn concentrations for pasture species tended to be on the gley soils, while highest concentrations were found on the YGE soils. The concentrations found in this survey are higher than those previously reported in New Zealand. Individual pasture species analysed by Whitton & Wells (1974) were 24 mg kg<sup>-1</sup> (range 12–49) for ryegrass, and 35 mg kg<sup>-1</sup> (range

13–63) for white clover, while those of a lower fertility grass, sweet vernal, averaged 30 mg kg<sup>-1</sup> (range 9–75). Towers (1977) found a mean concentration of 38 mg kg<sup>-1</sup> (range 25–50) for North Island pastures, while Metson et al. (1979) found mean concentrations of 28 mg kg<sup>-1</sup> (range 16–47) and 31 mg kg<sup>-1</sup> (range 20–50) for grass and clovers, respectively. The reasons for the higher Zn concentrations found in this survey are unclear.

### CONCLUSIONS

A survey of pastoral areas was undertaken to determine heavy metal accumulation in soils and pastures of both farmed and non-farmed sites over the major soil groups of the North and South Islands of New Zealand. Both soil and pasture samples were analysed for As, Cd, Cu, Pb, and Zn concentrations. Results showed that there was a significant enrichment of Cd in the top 7.5 cm of farmed soils over non-farmed soils. This enrichment was highly correlated to soil total P concentrations which in turn reflected phosphatic fertiliser inputs. Copper enrichment of soil has also occurred in the top 2.5 cm of farmed soils versus non-farmed soils, however this was not significant over the 0–7.5 cm depth. As Cu soil concentrations are typical of those found worldwide and Cu is an important element for both plant and animal nutrition, this accumulation is not considered a concern. Apart from a significant accumulation of As and Zn in the YBL and Zn in the BGL pastoral soils, there was no other accumulation determined in this survey, and the concentrations found were either typical of worldwide figures or in the lower range of those reported.

Dissection of pasture species into grass, legume, and weed components identified that the main difference between non-farmed and pastoral farms in heavy metal concentrations was in the weed species, although there was no clear relationship between soil metal levels and pasture species levels.

The elements measured did not exhibit the same enrichment in pastoral soils as had previously been found for Cd. Neither was there the decline in concentrations with depth as had been found for Cd, showing enhanced concentrations from phosphatic fertiliser applications. These two factors suggest that, unlike Cd, the concentrations of As, Cu, Pb, and Zn were essentially pedogenic in origin.

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