

**VG404**

**Total heavy metal status of horticultural  
soils in Queensland**

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**QLD Department of Primary Industries**



*Know-how for Horticulture™*

VG404

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## Table of Contents

	Page
<b>List of Figures</b> .....	ii
<b>List of Tables</b> .....	iii
<b>List of Appendices</b> .....	iv
<b>Executive Summary</b> .....	1
<b>Introduction</b> .....	3
Background .....	3
Literature Review .....	4
<i>Origin of heavy metals in soils</i> .....	4
<i>Total v extractable concentrations</i> .....	5
<i>Overseas data</i> .....	5
<i>Australian data</i> .....	7
<b>Methodology</b> .....	8
Sampling design, collection and pretreatment .....	8
Chemical and statistical analysis .....	9
<b>Results</b> .....	11
<b>Discussion</b> .....	17
Comparisons with other reported data .....	17
Regional differences and metal relationships .....	20
Effect of soil depth .....	22
Relationships with environmental soil quality guidelines .....	23
<b>Conclusions/Recommendations</b> .....	23
<b>References</b> .....	25
<b>Acknowledgements</b> .....	28

**List of Figures:**

<b>Figure No.</b>	<b>Page</b>
1. Location and distribution of soil sampling sites in Queensland.....	9
2. Regional median heavy metal concentrations in surface soils .....	14

**List of Tables:**

<b>Table No.</b>		<b>Page</b>
1.	Typical concentrations of heavy metals in world-wide agricultural soils.....	6
2.	Analytical data for certified reference materials.....	10
3.	Mean, median and ranges of heavy metal concentrations for three depths from Queensland horticultural soils.....	11
4.	Regional median heavy metal concentrations for three soil depths.....	13
5.	Effect of soil depth on heavy metal concentrations .....	16
6.	Correlation coefficients between heavy metal concentrations in surface soils .....	17
7.	Comparative overseas and other Australian heavy metal data and current soil quality guidelines with results for surface soils (0-10 cm) from this study .....	18

**List of Appendices:**

<b>Appendix No.</b>		<b>Page</b>
1.	Methods of analysis used in this study .....	<b>29</b>
2.	Lower limits of reporting for each metal used in this study .....	<b>29</b>

## EXECUTIVE SUMMARY

The objective of this study, funded by the Horticultural Research and Development Corporation, the Queensland Fruit and Vegetable Growers and the Department of Natural Resources, was to assess contemporary levels of a range of total heavy metal concentrations in a significant representation of Queensland soils subjected to normal horticultural practices. Carefully selected soils (three depths 0-10, 10-20, 20-30 cm) from 191 vegetable growing sites from an earlier Queensland wide survey provided an excellent opportunity to undertake this work at relatively low cost.

This report details total concentrations of eleven heavy metals [arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn)] found in horticultural soils, from seven districts across Queensland, compares their values with other reported heavy metal data, and discusses their possible modes of entry into the agricultural system.

Total concentrations of all heavy metals fell within typical ranges reported for world-wide soils, albeit in some cases at the higher end of what is termed 'common values'. When compared to world-wide mean values, the mean concentrations of Co, Cr, Cu, Ni and Zn were considerably higher, while As, Cd, Hg, Mo, Pb and Se were either lower or of similar value. For example, mean Co, Cr, Cu, Ni and Zn concentrations in the surface depth (0-10 cm) of these Queensland horticultural soils were 37, 132, 43, 88 and 76 mg/kg respectively, compared to corresponding world-wide means of 12, 84, 26, 34 and 60 mg/kg. In contrast, mean concentrations of Cd, Hg and Mo in the same surface soils were 0.195, 0.042 and 1.34 mg/kg respectively, compared to corresponding world-wide means of 0.62, 0.098 and 1.9 mg/kg.

Results from this study were comparable to other published heavy metal data on Australian agricultural soils, although in many cases again at the higher end of what is only limited available information. In particular, Cr concentrations were considerably higher than reported elsewhere for Australian soils. The median and arithmetic mean values of 0.035 and 0.042 mg Hg/kg respectively for 133 Queensland horticultural surface soils represent the first significant reporting of Hg concentrations in Australian agricultural soils.

While Cd levels were within typical ranges reported for other Australian soils, there is evidence to suggest this heavy metal was accumulating at a greater rate in these horticultural soils compared to that in southern and central Queensland canelands.

There were wide regional variations in soil heavy metal concentrations throughout Queensland. Arsenic concentrations were low with median values < 10 mg/kg in all soil depths from all districts. On the other hand, median concentrations (mg/kg) of Co (69), Cr (419) and Ni (353) in soils from the Mareeba/Atherton region were 23, 35 and 70 times higher respectively than corresponding heavy metal median values (3, 12 and 5) in soils from the Granite Belt area. The soils of the Mareeba/Atherton region also had the highest concentrations of Mo in all depths (approx. 1.9 mg/kg).

There is reasonable evidence for pedogenic processes being responsible for the wide range of Co, Cr and Ni concentrations. Similar patterns were evident for their relative order of distribution in surface soils between districts. Two samples from Mt. Isa contained the

highest concentrations of Cd, Cu, Hg, Pb and Zn suggesting a direct link to natural mineralisation and possible atmospheric deposition as a consequence to mining.

A positive and highly significant correlation ( $r = 0.59$ ,  $P < 0.01$ ) between total P and Cd implicated the use of P fertilisers as a significant source of Cd input to these horticultural soils. However, excluding Mt. Isa region, the highest median Cd concentration was found in surface soils from the Brisbane district (0.286 mg/kg) where there was no significant correlation between P and Cd. This suggests the soils from this region were either (a) more 'urban influenced' than those in other 'more rural' areas, and as such other more significant Cd sources contributing to them masked any Cd inputs from P fertilisers or (b) alternative P fertiliser sources low in Cd contributed to total P reserves.

Highly significant and positive correlation coefficients (0.89, 0.89 and 0.83) occurred between Ni and Co, Ni and Cr and Co and Cr respectively providing further support for their pedogenic associations. Other strong correlations existed between Se and Hg, Se and Mo, Cu and Zn, Cu and Cd, Pb and Cd, Pb and Cu and Pb and Mo. Unusually high Mo/Se ratios for median surface soil concentrations in the Granite Belt, compared to those in other areas, coupled with surface enrichment (1.15 mg/kg) of Mo relative to subsurface (0.78 mg/kg), suggested Mo inputs from anthropogenic origin were responsible.

Mean Cd, Cu, Pb and Zn concentrations decreased ( $P < 0.005$ ) with increasing depth across all districts. However, Cd was the only heavy metal whose concentrations were higher ( $P < 0.001$ ) in surface (0-10 cm) relative to subsurface depths (20-30 cm) within each district. In contrast, there was little effect of sampling depth on soil concentrations of Co, Cr, Ni and Se to 30 cm and this is consistent with minimal anthropogenic inputs of these elements and that such concentrations are mainly due to the parent materials from which the soils were derived.

Based on the current ANZECC/NHMRC (1992) environmental investigation threshold levels for heavy metals, a large proportion of the surface soils sampled in this study exceeded their relevant threshold levels. In particular, 66, 40 and 20 percent of samples tested for Cr, Ni and Cu respectively, exceeded the threshold levels currently set for these metals. Such results indicate that levels currently set in ANZECC/NHMRC (1992) are somewhat conservative for these heavy metals, and possibly Zn. There is justification therefore to raise the threshold levels to better reflect the normal background concentrations of these heavy metals that exist in Australian agricultural soils.

This study provides valuable new information on the regional distribution and contemporary background values of heavy metals in Queensland rural soils, particularly Cd, Co, Hg, Mo and Se. Such information provides a better understanding of the extent of existing accumulations of heavy metals in these soils and allows the horticultural industry to adopt appropriate management plans and develop sustainable practices on a more rational basis. It also has provided a substantial database of information which will not only be of benefit to the Queensland horticultural industry but also to Environmental and Health authorities by assisting them to formulate guidelines which relate to appropriate heavy metal levels in Australian soils.

## INTRODUCTION

### Background

The horticultural industry is Queensland's third largest rural sector with an annual production value of around \$1 billion (QDPI 1996) and therefore a major contributor to the Queensland economy. It occupies a wide geographical area of more than 30 000 ha of land with over 8 500 farm enterprises. Most produce is sold on the domestic market although the proportion being exported is increasing, particularly to Asian markets. Australian grown vegetables generally enjoy a 'clean green' reputation that needs to be maintained.

However, today more than ever, people are concerned about environmental pollution, particularly when it impacts on food and water quality. Community awareness of heavy metals, as toxic environmental contaminants, is increasing and their concentrations and distribution in soils have a significant importance because of the key role soils have in supplying these contaminants to the human and animal food chain. Heavy metals accumulate in soils from a number of external contaminating sources as well as being governed by the pedogenesis of the parent rock material. This soil formation process can produce vastly different metal concentrations in soil derived from the same parent material (Tiller 1989; Fergusson 1990). Therefore, to gain a reliable guide to the heavy metal content of soils, knowledge of the parent material should be considered *together* with inputs from anthropogenic sources.

It is important to distinguish between the natural or background concentrations of heavy metals in soils and those added through anthropogenic sources since it allows an estimation of the extent of pollution (Kabata-Pendias 1991). This distinction however, can be very difficult to make for many trace elements but knowledge of contemporary soil heavy metal levels will assist in identifying possible areas of contamination and their sources of pollution.

Because heavy metals are both persistent in soils and not bio-degradable, they are a major cause of land contamination under Queensland's Contaminated Land Act (1991). Heavy metal inputs from anthropogenic sources could be contaminating Queensland's horticultural soils leading to increased metal concentrations in the food chain which result in their accumulation in the human body, with cadmium (Cd), mercury (Hg) and lead (Pb) being of particular concern.

While there are many reports on heavy metal concentrations in overseas soils, there is much less of this information available for Australian soils, particularly in Queensland and for those derived from horticultural practices. This report details results of an extensive survey to assess contemporary levels of a range of total heavy metals [arsenic (As), Cd, cobalt (Co), chromium (Cr), copper (Cu), Hg, molybdenum (Mo), nickel (Ni), Pb, selenium (Se) and zinc (Zn)] in horticultural soils of Queensland. Carefully selected soils (three depths) from a recent state Cd bio-availability survey (Rayment 1994), representing a significant proportion of horticultural soils in Queensland, provided an opportunistic occasion to gain this information at relatively low cost. This survey had revealed higher-than-desirable levels of extractable Cd in some soils while a few crops violated the Maximum Permitted Concentration (MPC) for Cd listed in the Australian Food Standard. Also, Mo and occasionally Cu and Zn were at elevated concentrations in the edible portions of several vegetables (Rayment 1994 a).

## Literature Review

### *Origins of heavy metals in soils*

Heavy metals as toxic environmental contaminants are receiving more attention in recent times in response to increasing public concern that their presence in the environment is a major factor in placing ecosystems at risk. There is often a narrow range between elemental concentrations found to be essential to humans and animals and those considered toxic causing adverse health effects (eg. Se). Moreover, the level of toxicity depends on the degree and type of adverse effect. For metals and metalloids, toxicity is also governed by chemical form. For example, organo-As compounds are less toxic than inorganic ones (O'Neill 1990) whereas, of all forms of Hg, methyl-Hg is the most toxic (Steinnes 1990). In general, water soluble forms of heavy metals have greater toxicity, including higher rates of absorption following ingestion, than do sparingly soluble or insoluble compounds.

Soils are a major sink for heavy metals. The origins of heavy metals in soils arise from the weathering processes on their relevant parent rock materials and through inputs of pollutants from various external sources. The concentrations originating from pedogenic processes can be quite variable depending on the type of parent rock material. There are numerous references to heavy metal concentrations of major rock types (Ure and Berrow 1982; Alloway 1990) but generally, soils derived from igneous and sedimentary rocks contain higher concentrations of heavy metals relative to those formed from sandstone. Therefore variable natural background concentrations of heavy metals in soils are often a reflection of their extremes in parent rock materials.

The anthropogenic sources of heavy metals in soils are through the use of fertilisers, particularly phosphatic ones, pesticides, sewage sludges and organic manures as well as those added from atmospheric emissions (factory and power stations; leaded petrol; mining and smelting operations). While the latter sources of pollution are more difficult to control locally, inputs from the former ones can be more easily regulated from the knowledge of both rate of application of fertilisers or organic wastes and the contaminant concentration in them. In agricultural and horticultural soils, phosphate fertilisers, sewage sludges and refuse-derived composts provide the major sources of many heavy metals. For example, Rayment *et al.* (1989) reported concentrations of Cd in phosphatic fertilisers, expressed as mg Cd per kg of P, of  $413 \pm 39.7$ . In fact, estimates of anthropogenic inputs of Cd to soils in western countries (Alloway 1990) are: phosphatic fertilisers 54-58%, atmospheric deposition 39-41% and sewage sludge 2-5%. Rayment (1994) has estimated that Cd inputs from phosphate fertilisers to soils in Queensland with a long history of vegetable production probably exceed 0.047 kg Cd/ha. These additions correspond to a soil Cd concentration of at least 0.047 mg/kg to a depth of 10-15 cm. Because sewage sludges can contain significant concentrations of heavy metals, many countries have developed guidelines for their use on land (USEPA 1993; NSW EPA 1996) ensuring ecologically sustainable metal loading rates to soils.

Such anthropogenic inputs of heavy metals to agricultural lands can be far greater than losses resulting in gradual accumulation in soils. For example, Merry and Tiller (1991) estimate that extractable Cd concentrations in surface soils in an agricultural region near Adelaide will

double within about 20 years, if current fertiliser and atmospheric inputs are maintained. On the other hand, 200 years would be required for similar increases in soil Pb.

#### *Total v extractable concentrations*

When determining heavy metal concentrations in soils the analytical method chosen should be dependent on the purpose for which the analytical data are required. If the extent of pollution of a soil by heavy metals is required then the measurement of their total concentration is determined. This can provide an assessment of the base-line or background situation, a measure of the total pool of heavy metals, as well as unequivocal evidence of changes in soil composition of heavy metals produced by pollution, plant uptake or agricultural practices. Furthermore, the definition of 'total' analysis should be clearly understood e.g. whether acid digestion (including acid composition) or x-ray fluorescence, a non-destructive method.

In contrast, total concentrations do not generally provide a reliable guide to the biological effectiveness, toxicity or mobility of a metal. Various extractants have been used to estimate the plant available fraction of the heavy metal content of a soil (Lindsay and Norvell 1978; Beckett 1989; Alloway 1990). Rayment (1994) found that soil Cd extracted in 0.1 M CaCl<sub>2</sub> generally proved to be a better, more consistent predictor of soil-Cd bio-availability to Queensland grown vegetables across the mostly acidic soils studied than did soil Cd extracted by either 1.0 M HCl, 0.005 M DTPA or 0.05 M EDTA. However, correlations for some vegetables were disappointing mainly due to the low Cd uptake by these vegetables across a relatively wide range of soil Cd concentrations.

#### *Heavy metal concentrations in soils - overseas data*

There are many overseas studies which report total heavy metal contents of soils, particularly in Great Britain, Europe and the USA. The data in Table 1, reported by Alloway (1990), indicate the ranges of heavy metals found in agricultural soils subjected to normal agricultural practices. These levels are in general agreement with other data reported for world-wide soils not particularly subjected to heavy pollution (Ure and Berrow 1982; Fergusson 1990).

**Table 1** Typical concentration ranges of heavy metals (mg/kg, dry wt) in worldwide agricultural soils.

Element	Range	Common Value
As	0.1 - 50	1 - 20
Cd	0.01 - 2.4	0.2 - 1.0
Co	1 - 40	10
Cr	5 - 1500	70 - 100
Cu	2 - 250	20 - 30
Hg	0.01 - 0.3	0.03 - 0.06
Mo	0.2 - 5	1 - 2
Ni	2 - 1000	50
Pb	2 - 300	10 - 30 rural 30 - 100 urban
Se	0.01 - 2	0.5
Zn	10 - 300	50

Source: Alloway (1990)

One of the most extensive surveys involving the analysis of 'total' concentrations (aqua regia soluble) of heavy metals in soils was undertaken in England and Wales ( McGrath 1986; McGrath and Loveland 1991). Chemical analyses for 16 elements were performed on approximately 6000 samples of topsoils providing excellent knowledge of the regional distribution and contemporary background values of metals. Furthermore, such data became useful in the setting of limits for environmental protection purposes. Median concentrations of selected heavy metals Cd, Cr, Cu, Ni, Pb and Zn were 0.7, 39, 18, 23, 40 and 82 mg/kg (air dry basis) respectively. Davies and Paveley (1985) reported on the findings of a study of total concentrations of metals in soils from throughout Wales. Their work led to the preparation of soil metal maps as well as allowing better estimates of the normal range of metal levels in soils. Reported median concentrations for a number of heavy metals in 654 Welsh surface soils were : Cd 0.3, Co 7, Cu 12, Ni 14, Pb 35 and Zn 63 mg/kg (air dry basis).

Comparisons between total heavy metal concentrations in virgin/native soils and agricultural soils was used to examine the extent of heavy metal contamination in New Zealand (Roberts *et al.* 1996). From a survey involving 312 pastoral farm sites and 86 native sites, soils (0 - 7.5 cm depth) were analysed for As, Cd, Cu, Pb and Zn with arithmetic mean values (native sites) of 4.3, 0.19, 17, 13.3 and 65 mg/kg respectively while mean concentrations of corresponding metals in pastoral soils were 4.9, 0.44, 17.7, 11.7 and 68 mg/kg respectively. Of the heavy metals studied only Cd appeared to have been enriched in the pastoral soils which was attributed to the use of phosphatic fertilisers.

With increasing interest in land application of sewage sludges (biosolids), and concerns for sludge-derived heavy metals to enter the human and animal food-chain, Pierce *et al.* (1982) undertook an investigation to establish contemporary base-line heavy metal concentrations in

soils. They determined concentrations of total Cd, Cr, Cu, Ni, Pb and Zn in surface soils of 16 soil series in Minnesota (USA) and found mean values of 0.39, 39, 23, 18, <25 and 60 mg/kg respectively. Such studies provide important information on the metal content of soils at potential sites for biosolids application.

Holmgren *et al.* (1993) reported on the findings from a USDA, FDA and USEPA initiated study to determine contemporary background levels of heavy metals in soils subjected to normal agricultural practices. Such information, coupled with corresponding metal levels in crop samples, was considered an important step in determining acceptable dietary metal levels, particularly Cd and Pb, in teenage males. There was some concern that these dietary levels were already too high and would further increase with cropland application of sewage sludge and P fertilisers. Median concentrations in 3045 surface soils of Cd, Cu, Ni, Pb and Zn were 0.2, 18.5, 18.2, 11 and 53 mg/kg (dry weight basis) respectively.

#### *Heavy metal concentrations in soils - Australian data*

In Australia, the creation of various State Environmental Protection Agencies or State Environmental Departments initiated studies leading to the development of guidelines for the assessment and management of contaminated sites. This in turn led to studies being undertaken to determine contemporary background concentrations of heavy metals in Australian agricultural and urban soils. In his paper on urban soil contamination in Australia, Tiller (1992) also collated published and unpublished data on concentrations of a number of potentially toxic elements in Australian rural surface soils (Table 7). He stated that the reasons why the highest "background" concentrations of Co, Cu, Mo, Ni and Pb found in these Australian soils exceeded those quoted for Dutch soils were due to the great range of soil parent materials and the kind and duration of soil-forming processes existing in Australia compared to the Netherlands. Another significant factor was the differences in contaminants associated with the more intensive Dutch agricultural activity. This suggests a cautious approach in adopting soil-based criteria developed for different soils and climates.

Other Australian studies have reported heavy metal concentrations in soils in an endeavour to characterise the range and type of these potential contaminants in rural and urban lands (Merry and Tiller 1991; Olszowy *et al.* 1993). The former study reported mean Cd concentrations in surface soils (0-5 cm) near Adelaide of 0.11, 0.18, 0.26 and 0.09 mg/kg for never-agricultural, pasture, orchard and exotic forest soils respectively. The study by Olszowy *et al.* (1993) involved the analysis of 320 surface soils from urban areas in four Australian capital cities and 120 surface soils from rural locations around the Brisbane area believed to be undisturbed by human activity. The Queensland data in this report represented the first published information on background "total" concentrations of heavy metals in soils from that State in recent times. Results indicated that, for the Queensland rural soils studied, Mn was the only element to exceed the ANZECC/NHMRC (1992) environmental investigation threshold of 500 mg/kg. Geometric mean values for As and Ni were similar for both rural and urban soils while urban soils had higher mean values for Cr, Cu, Pb and Zn. Unfortunately, the detection limits for Cd and Hg were too high in this study to allow statistical comparisons, with most samples being below the analytical report limit.

While the study by Olszowy *et al.* (1993) indicated relatively low concentrations of heavy metals in Queensland rural soils presumed to be undisturbed by human activity, Barry and Rayment (1992) found considerably higher concentrations of a number of metals in surface

'soils' of Raine Island, a 30 ha coral cay on the far northern area of the Great Barrier Reef. There are, however, reasonable grounds to suggest that the elevated arithmetic mean concentrations (mg/kg, air-dry weight basis) of Cd (37), Cu (76), Se (10) and Zn (502) in these 'soils' are a natural phenomenon rather than a consequence of anthropogenic contamination.

The earliest published data found on heavy metal concentrations in Queensland soils were reported by Giles (1959) and Oertel and Giles (1959). The former study found median concentrations (mg/kg) of heavy metals in 118 surface soils from various soil groups to be Co (16), Cu (35), Mo (7.1) and Zn (53).

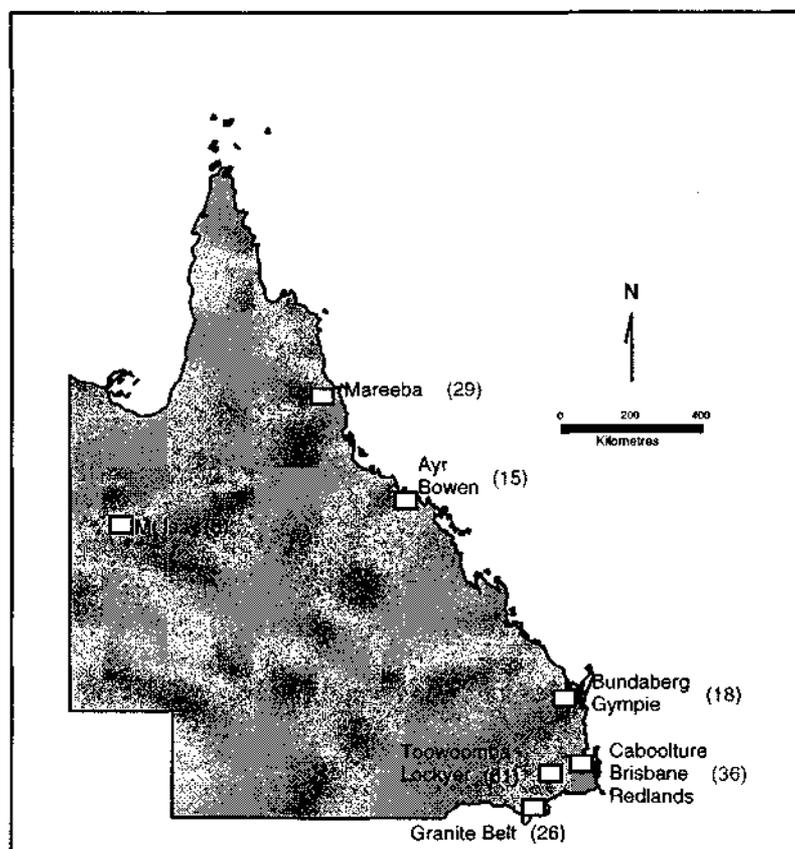
A number of studies on the relationships between soil and vegetable heavy metal concentrations have shown variable results (Wiersma *et al.* 1986; Alegria *et al.* 1991) indicating, once again, the importance of carrying out such studies under local environmental conditions.

Clearly there is far more data on heavy metal concentrations in overseas soils than for Australian soils, with very limited information on Queensland soils in particular. There has been few studies where normal or background heavy metal concentrations in Australian soils have been determined making it difficult to assess the real impact of agricultural practices. Phosphatic fertilisers have provided the main anthropogenic source of Cd to both Australian and overseas agricultural soils while other causes of variable heavy metal concentrations are a reflection of the extremes in parent rock materials from which the soils are derived.

## METHODOLOGY

### Sampling design, collection and pretreatment

Soil samples had been collected between August 1989 and mid-1991 for an earlier study (Rayment 1994) which examined the extent to which Cd was accumulating in edible portions of Queensland-grown vegetables and their associated soils in which they were grown. The field survey involved the collection of carefully selected soils from three depths (0-10, 10-20 and 20-30 cm) at 191 sites located in the major vegetable growing areas of Queensland. A greater intensity of sampling occurred at sites where the most common or more important types of vegetables were grown. The more intensive component involved eight vegetable types each with three within-paddock sampling sites at six or seven farms across Queensland. For the low intensity component, eleven vegetable types and different from those in the more intensive one, were each sampled at one site from three or four farms. The spread of sampling sites essentially came from seven districts in Queensland and these are shown in Figure 1.



**Figure 1: Location and number per district (in parenthesis) of soil sampling sites in Queensland**

At each sampling site a pit approx. 30 cm wide and 30 cm deep was dug across the crop row. A vertical slice was taken across the face of the pit from each depth interval and placed into a clean polyethylene bag. Samples were collected immediately prior to or during commercial harvest. All sites selected for sampling had been subjected to normal horticultural practices with no other known potential anthropogenic inputs of heavy metals, excluding possibly a site at Mt. Isa (reasons for this are detailed later in the report). Protocols used for soil sampling included use of stainless steel implements, poly-gloves and coats which ensured the minimisation of any accidental heavy metal contamination during sampling and transport to the laboratory.

At the laboratory, each sample was thoroughly mixed and a subsample taken for metal analysis. This was dried at 40°C in a stainless steel lined oven, then passed through an acid washed plastic 2 mm sieve. Each sample was subsequently ground to < 50 µm using a shatter-box grinding mill equipped with a stabilised zirconia grinding head and stored in a sealed acid washed plastic container prior to analysis.

### Chemical and statistical analyses

Chemical analyses for heavy metals, excluding Mo, were undertaken in the laboratory of what is now the Resource Sciences Centre, Indooroopilly, Queensland Department of Natural Resources. Molybdenum was determined in acid digest solutions provided to the DPI's

Animal Health Laboratory, Yeerongpilly. Details of the analytical methods used and the lower limits of reporting (LOR) are summarised in Appendices 1 and 2 respectively. To ensure heavy metal analytical techniques were appropriate, two Certified Reference Materials, namely NRC BCSS-1 (a marine sediment) and BCR 142 (a light sandy soil), were analysed on several occasions and the results, shown in Table 2, indicate most metals were within expected certified values. The results for Cd and Hg, based on a nitric/hydrochloric acid extraction, confirm the findings of Louie *et al.* (1993) that this method has the ability to extract close to the "real total" concentrations of these two heavy metals. Additional quality assurance was provided by including two 'in-house' secondary reference soils in each analytical run.

For the purposes of calculating means and medians, where concentrations were below the LOR, a value of half the relevant LOR was used. Correlation coefficients (*r*) were determined for simple linear relationships between elements. Arithmetic means, medians and standard deviations were calculated on untransformed data. For some data sets, the skewed distribution of data were normalised using transformations as appropriate and comparisons made using the 'paired' student *t* test.

**Table 2 Mean ( $\pm$ SD) concentrations of heavy metals (mg/kg, dry wt) obtained for certified reference materials**

Element	BCSS-1		BCR-142	
	This study	Cert value	This study	Cert value
As	10.3 $\pm$ 0.4(10) <sup>b</sup>	11.1 $\pm$ 1.4	14.7 $\pm$ 0.4(6)	16.5 <sup>a</sup> $\pm$ 2.0
Cd	0.26 $\pm$ 0.02(12)	0.25 $\pm$ 0.04	0.24 $\pm$ 0.02(14)	0.25 $\pm$ 0.09
Co	13.5 $\pm$ 2.8(8)	11.4 $\pm$ 2.1	10.0 $\pm$ 1(3)	7.9 <sup>a</sup> $\pm$ 1.1
Cr	121 $\pm$ 8(8)	123 $\pm$ 14	80 $\pm$ 6(3)	74.9 <sup>a</sup> $\pm$ 9.4
Cu	21.0 $\pm$ 2.6(8)	18.5 $\pm$ 2.7	29.5 $\pm$ 1.1(3)	27.5 $\pm$ 0.6
Hg	-	-	0.108 $\pm$ 0.022(8)	0.104 $\pm$ 0.012
Mo	1.8 $\pm$ 0.1(2)	(1.9) <sup>a</sup>	-	-
Ni	58 $\pm$ 7(8)	55.3 $\pm$ 3.6	32 $\pm$ 2(3)	29.2 $\pm$ 2.5
Pb	24 $\pm$ 4(8)	22.7 $\pm$ 3.4	39 $\pm$ 4(3)	37.8 $\pm$ 1.9
Se	0.46 $\pm$ 0.04(11)	0.43 $\pm$ 0.06	0.55 $\pm$ 0.04(6)	0.53 <sup>a</sup> $\pm$ 0.12
Zn	121 $\pm$ 19(8)	119 $\pm$ 12	99 $\pm$ 10(3)	92.4 $\pm$ 4.4

<sup>a</sup> indicative value

<sup>b</sup> number in parenthesis refers to number of analyses

## RESULTS

Table 3 presents the arithmetic mean, median and range for the total concentrations of heavy metals found in three depths of selected horticultural soils in Queensland. The analyses for Mo and Se were performed on all surface soils, and subsoils from only one of the three within-paddock sites selected from the intensive sampling component. Mercury analysis, an addition to the proposed analytical suite for the project, was carried out on surface soils mainly from one of the three within-paddock sites from the intensive sampling component as well as on surface soils from the less intensive component.

**Table 3 Arithmetic mean ( $\pm$  SD) and median concentrations and ranges of heavy metals (mg/kg, dry wt) for three depths from selected horticultural soils of Queensland.**

Metal	Depth (cm)	No. Samples	Range	Median	Mean ( $\pm$ Standard Deviation)
As	0-10	191	1 - 20	2	3 (3)
	10-20	190	1 - 24	1	3 (3)
	20-30	186	1 - 31	2	3 (4)
Cd	0-10	191	0.016 - 2.08	0.125	0.195 (0.238)
	10-20	190	<0.01 - 1.95	0.115	0.167 (0.211)
	20-30	186	<0.01 - 2.17	0.071	0.110 (0.203)
Co	0-10	191	<6 - 165	26	37 (38)
	10-20	190	<6 - 155	26	37 (38)
	20-30	186	<6 - 154	27	35 (36)
Cr	0-10	191	<9 - 573	65	132 (135)
	10-20	190	<9 - 598	68	134 (136)
	20-30	186	<9 - 607	67	132 (135)
Cu	0-10	191	<8 - 148	38	43 (31)
	10-20	190	<8 - 149	37	42 (30)
	20-30	186	<8 - 145	34	37 (29)
Hg	0-10	133	<0.006 - 0.155	0.035	0.042 (0.030)
	10-20	6	0.034 - 0.127	0.055	0.069 (0.033)
	20-30	6	0.038 - 0.126	0.060	0.068 (0.032)
Mo	0-10	191	0.20 - 5.17	1.01	1.34 (0.95)
	10-20	52	0.20 - 3.41	1.00	1.30 (0.85)
	20-30	51	0.21 - 3.10	0.90	1.22 (0.78)
Ni	0-10	191	<10 - 439	27	88 (117)
	10-20	190	<10 - 452	27	89 (118)
	20-30	186	<10 - 451	27	86 (114)
Pb	0-10	191	5 - 81	24	27 (15)
	10-20	190	<4 - 112	23	27 (15)
	20-30	186	4 - 221	22	27 (20)
Se	0-10	191	<0.05 - 3.6	0.28	0.37 (0.44)
	10-20	52	<0.05 - 3.3	0.30	0.38 (0.46)
	20-30	51	<0.05 - 3.2	0.30	0.39 (0.45)
Zn	0-10	191	<12 - 263	73	76 (48)
	10-20	190	<12 - 270	70	75 (48)
	20-30	186	<12 - 262	62	68 (49)

In all cases, but particularly for Cd, Co, Cr, Mo, Ni and Se, the arithmetic mean values were much greater than the median values. This skewness probably reflects the vastly different regional geology and parent materials from which the soils are derived. This would apply especially for Co, Cr, Mo, Ni and Se - heavy metals which are not generally attributed to anthropogenic inputs. The overall results for Cd, a heavy metal well known for its anthropogenic contribution to soils from phosphate fertilisers (Alloway 1990; Rayment 1994), were especially influenced by data from one intensively sampled site in Mt. Isa (three within-paddock results for each depth). In this case, the site's short distance from the mine on the downward side of the prevailing winds, suggested the soil had possibly been affected by atmospheric deposition from nearby mining activity. If this data is excluded, the mean Cd values for the three depths down the profile become 0.171, 0.145 and 0.087 mg/kg respectively, while the median values remain the same. Moreover, the maximum Cd concentration across the other six districts was 0.748 mg/kg in a surface (0 - 10 cm) soil.

The range of concentrations of most heavy metals varied considerably between districts. Table 4 lists the median concentrations, together with sample numbers, of heavy metals for each depth within each of the seven districts. Sample numbers from each district varied from six at Mt. Isa to 61 in the Lockyer / Fassifern / Toowoomba area.

Arsenic concentrations were low with median values < 10 mg/kg in all soil depths from all districts. On the other hand, median concentrations (mg/kg) of Co (69), Cr (419) and Ni (353) in soils from the Mareeba/Atherton region were 23, 35 and 70 times higher respectively than corresponding heavy metal median values (3, 12 and 5) in soils from the Granite Belt area. The soils of the Mareeba/Atherton region also had the highest concentrations of Mo in all depths (approx. 1.9 mg/kg). The limited sampling from Mt. Isa contained the highest concentrations of Cd, Cu, Hg, Pb and Zn, which may reflect the natural mineralisation of the area and possible atmospheric deposition. Excluding the Mt. Isa district, the highest median concentration of Hg (0.065 mg/kg) was found in surface soils from the Bundaberg/Gympie area, the same district which produced the highest concentrations of soil Se. Soils from the Brisbane and surrounding districts contained the highest concentrations of Cd, again excluding Mt. Isa data.

A more evident representation of the median concentrations of heavy metals in the surface soils (0-10 cm) within each district, together with associated range bars, is shown in Figure 2. Similar patterns of heavy metal distribution across districts emerge. For example, the relative order of decreasing median concentrations of Co, Cr and Ni is district 1 > 3 > 5=6=2 > 4 > 7, while Hg and Se also show other similar patterns between themselves.

**Table 4** Median heavy metal concentrations (mg/kg, dry wt) for three soil depths from each district

Metal	Depth (cm)	District code <sup>A</sup>						
		1	2	3	4	5	6	7
As	0-10	1 (29) <sup>B</sup>	1 (15)	1 (61)	6 (36)	3 (18)	6 (6)	4 (26)
	10-20	1 (29)	1 (14)	1 (61)	7 (36)	2 (18)	6 (6)	4 (26)
	20-30	1 (24)	1 (15)	1 (61)	5 (36)	2 (18)	5 (6)	4 (26)
Cd	0-10	0.096 (29)	0.082 (15)	0.140 (61)	0.184 (36)	0.120 (18)	0.696 (6)	0.096 (26)
	10-20	0.095 (29)	0.075 (14)	0.127 (61)	0.170 (36)	0.117 (18)	0.701 (6)	0.080 (26)
	20-30	0.044 (24)	0.032 (15)	0.087 (61)	0.097 (36)	0.061 (18)	0.582 (6)	0.067 (26)
Co	0-10	69 (29)	13 (15)	51 (61)	5 (36)	26 (18)	28 (6)	3 (26)
	10-20	70 (29)	14 (14)	52 (61)	5 (36)	25 (18)	28 (6)	3 (26)
	20-30	66 (24)	13 (15)	52 (61)	5 (36)	21 (18)	30 (6)	3 (26)
Cr	0-10	419 (29)	59 (15)	156 (61)	40 (36)	61 (18)	55 (6)	12 (26)
	10-20	431 (29)	62 (14)	160 (61)	40 (36)	61 (18)	55 (6)	12 (26)
	20-30	388 (24)	64 (15)	159 (61)	41 (36)	62 (18)	57 (6)	9 (26)
Cu	0-10	52 (29)	14 (15)	42 (61)	35 (36)	31 (18)	109 (6)	21 (26)
	10-20	51 (29)	15 (14)	39 (61)	34 (36)	24 (18)	106 (6)	18 (26)
	20-30	54 (24)	15 (15)	39 (61)	21 (36)	27 (18)	96 (6)	13 (26)
Hg <sup>c</sup>	0-10	0.027 (11)	0.011 (7)	0.042 (41)	0.031 (28)	0.065 (14)	0.075 (6)	0.020 (26)
Mo	0-10	1.94 (29)	0.35 (15)	0.98 (61)	1.25 (36)	0.93 (18)	0.75 (6)	0.98 (26)
	10-20	1.94 (9)	0.34 (4)	1.00 (17)	1.32 (9)	0.96 (5)	0.74 (2)	1.08 (6)
	20-30	1.88 (8)	0.4 (4)	0.90 (17)	1.48 (9)	0.96 (5)	0.66 (2)	0.78 (6)
Ni	0-10	353 (29)	16 (15)	106 (61)	6 (36)	27 (18)	33 (6)	5 (26)
	10-20	344 (29)	16 (14)	108 (61)	7 (36)	26 (18)	32 (6)	5 (26)
	20-30	219 (24)	18 (15)	109 (61)	7 (36)	28 (18)	35 (6)	4 (26)
Pb	0-10	31 (29)	14 (15)	24 (61)	19 (36)	23 (18)	49 (6)	26 (26)
	10-20	28 (29)	14 (14)	22 (61)	18 (36)	24 (18)	52 (6)	27 (26)
	20-30	30 (24)	14 (15)	22 (61)	15 (36)	23 (18)	40 (6)	27 (26)
Se	0-10	0.35 (29)	0.08 (15)	0.38 (61)	0.30 (36)	0.45 (18)	0.23 (6)	0.08 (26)
	10-20	0.36 (9)	0.085 (4)	0.40 (17)	0.32 (9)	0.50 (5)	0.24 (2)	0.09 (6)
	20-30	0.35 (8)	0.10 (4)	0.40 (17)	0.47 (9)	0.46 (5)	0.22 (2)	0.08 (6)
Zn	0-10	58 (29)	38 (15)	119 (61)	53 (36)	24 (18)	179 (6)	26 (26)
	10-20	58 (29)	41 (14)	116 (61)	47 (36)	23 (18)	172 (6)	22 (26)
	20-30	57 (24)	40 (15)	110 (61)	31 (36)	19 (18)	150 (6)	15 (26)

<sup>A</sup> District 1 = Atherton/Mareeba; District 2 = Ayr/Bowen; District 3 = Lockyer/Fassifern/Toowoomba; District 4 = Brisbane/Caboolture/Redlands; District 5 = Bundaberg/Gympie; District 6 = Mt. Isa; District 7 = Granite Belt

<sup>B</sup> number in parenthesis refers to number of samples

<sup>C</sup> mercury data for surface (0-10 cm) soils only

**Figure 2: Regional median concentration, with associated range bars, of heavy metals in surface (0-10cm) soils.**

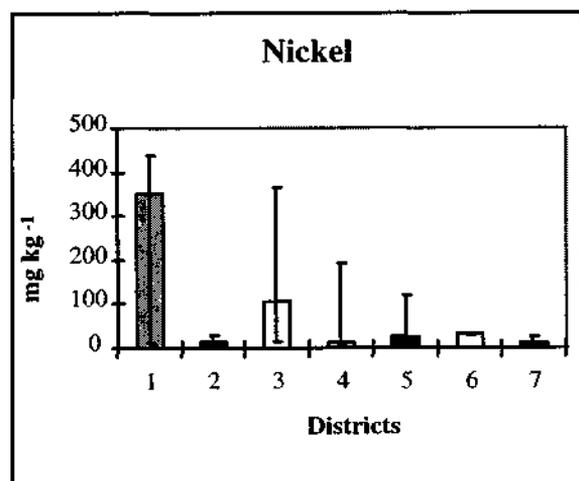
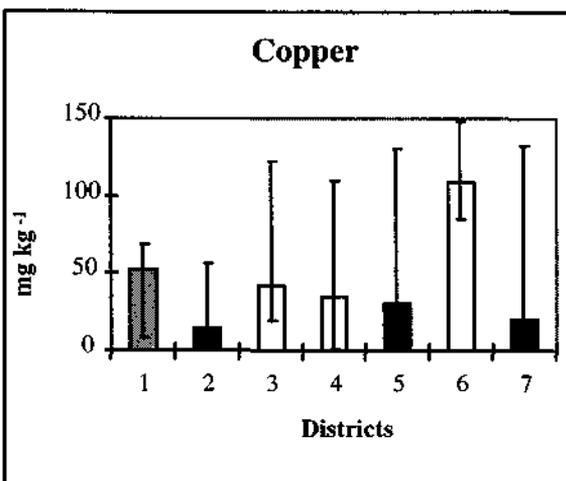
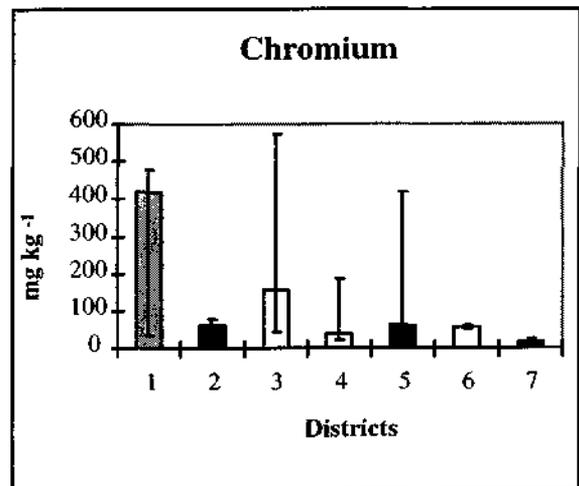
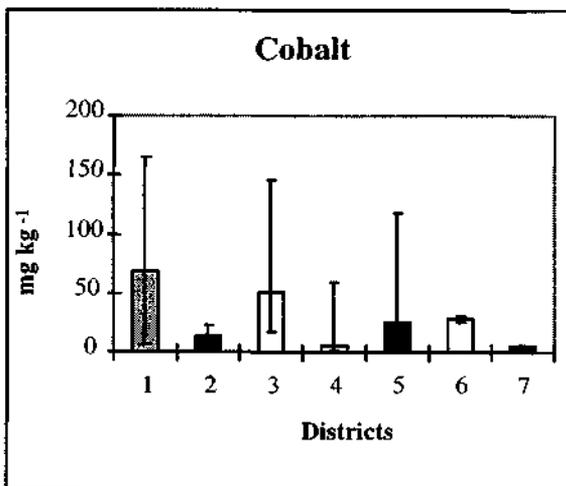
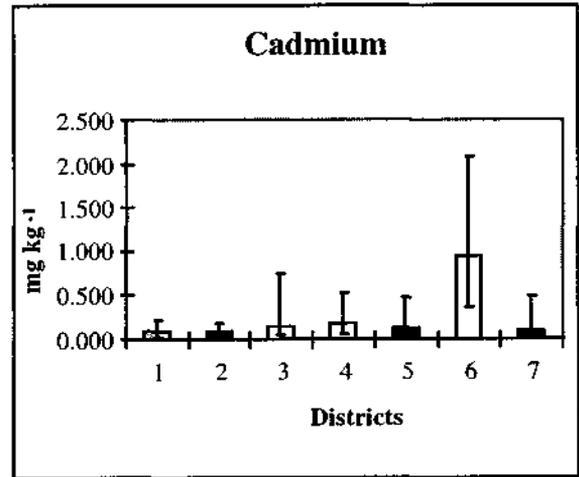
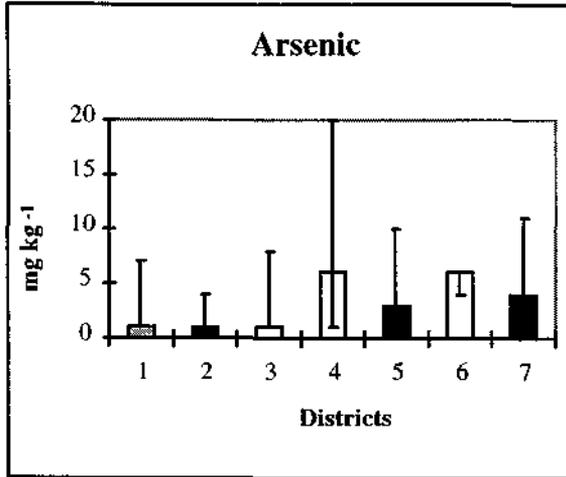
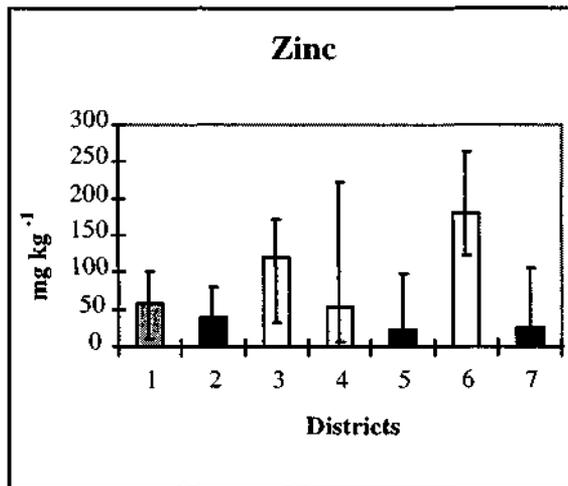
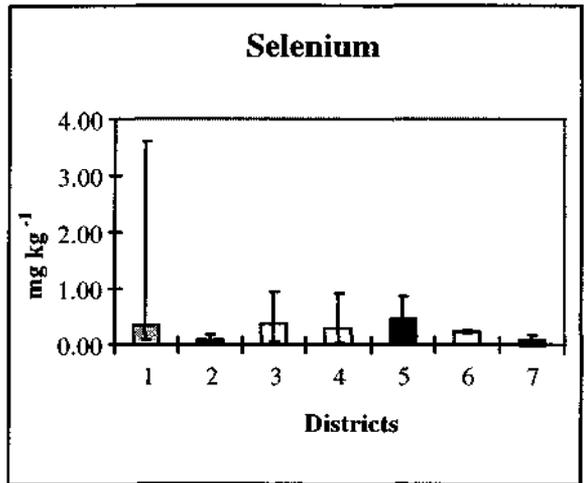
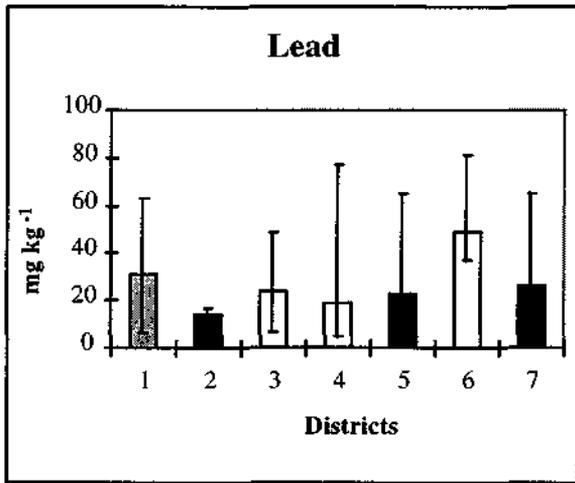
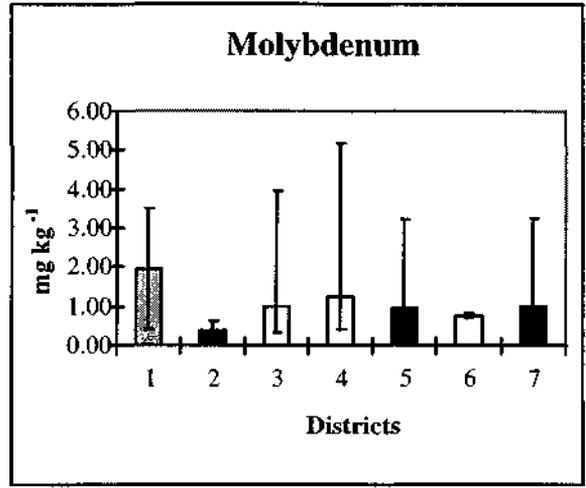
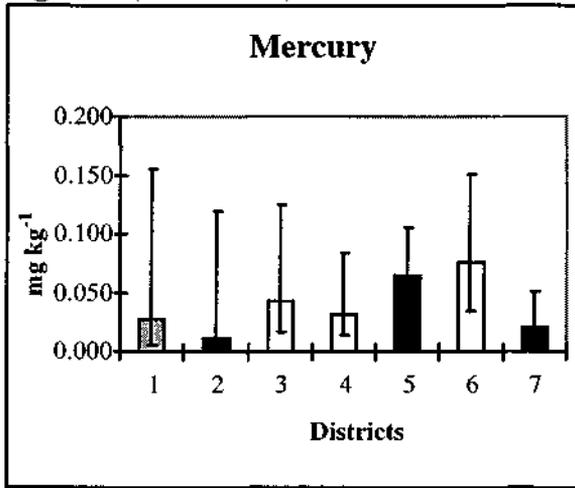


Figure 2 (Continued):



District 1 = Atherton/Mareeba; District 2 = Ayr/Bowen; District 3 = Lockyer/Fassifern/Toowoomba; District 4 = Brisbane/Caboolture/Redlands; District 5 = Bundaberg/Gympie; District 6 = Mt. Isa; District 7 = Granite Belt

Table 5 shows the 'paired' arithmetic mean concentrations of heavy metals for surface (0-10 cm) and subsurface (20-30 cm) depths for all districts. The skewed distribution of the data was normalised by transformations (see Table 5), then probabilities examined for significance based on the Student t test. No consistent trends among heavy metals occurred with depth. Mean concentrations of Cd, Cu, Pb and Zn decreased (all  $P < 0.05$ ) with increasing depth, while there was no significant effect of depth on concentrations of all other metals across all districts. Furthermore, Cd was the only heavy metal to decrease ( $P < 0.001$ ) in concentration with increasing depth within each district. Mean concentrations of Cu and Zn decreased ( $P < 0.05$ ) with depth in all districts excluding Mareeba/Atherton and Ayr/Bowen. Mean Pb concentrations in surface soils (0-10 cm) from 'paired' sites in Lockyer/Fassifern/Toowoomba and Brisbane and surrounding districts were higher ( $P < 0.05$ ) than concentrations in corresponding subsurface soils from these areas.

**Table 5** Effect of depth on arithmetic mean concentrations (mg/kg, dry wt) of total heavy metals in Queensland horticultural soils.

Heavy Metal	Number of Paired Data	Mean Concentrations $\pm$ SD		P <sup>a</sup>
		0 - 10 cm	20 -30 cm	
As	186	3 $\pm$ 3	3 $\pm$ 4	0.13
Cd	186	0.198 $\pm$ 0.241	0.110 $\pm$ 0.203	<0.001
Co	186	35.6 $\pm$ 37	35 $\pm$ 36	0.35
Cr	186	128.5 $\pm$ 131	132 $\pm$ 135	0.92
Cu	186	43.6 $\pm$ 31	37 $\pm$ 29	<0.001
Mo	51	1.29 $\pm$ 0.88	1.22 $\pm$ 0.79	0.13
Ni	186	84.3 $\pm$ 113	86 $\pm$ 114	0.45
Pb	186	27.4 $\pm$ 15	26.7 $\pm$ 20	0.004
Se	51	0.37 $\pm$ 0.46	0.39 $\pm$ 0.46	0.11
Zn	186	77.2 $\pm$ 49	67.7 $\pm$ 48.5	<0.001

<sup>a</sup> Probabilities for significance based on student t test using transformed data for each heavy metal. Transformations were  $2A/(A+B)$  and  $2B/(A+B)$ , where A is the concentration of the 0-10cm sample and B is the concentration of the corresponding 20-30 cm profile segment.

Correlation coefficients for simple linear relationships between metal concentrations in surface soils across all districts are shown in Table 6. The majority were positive and significant ( $P < 0.05$  or better). By far the best correlation coefficients (0.89, 0.89 and 0.83) occurred between Ni and Co, Ni and Cr and Co and Cr respectively. Other strong correlations existed between Se and Hg, Se and Mo, Cu and Zn, Cu and Cd, Pb and Cd, Pb and Cu and Pb and Mo. Relatively strong negative correlations occurred between As and the three elements Co, Cr and Ni although the concentration range for As was limited.

**Table 6** Correlation coefficients<sup>1</sup> (r) for simple linear relationships between metals in surface horticultural soils of Queensland - (n= 191, excluding Hg metal comparisons where n = 133)

Metal (X variable)	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
As											
Cd	0.16										
Co	-0.36	0.03									
Cr	-0.41	0.01	0.83								
Cu	0.08	0.54	0.47	0.43							
Hg <sup>2</sup>	0.16	0.44	0.30	0.18	0.41						
Mo	0.16	0.20	0.29	0.31	0.39	0.35					
Ni	-0.38	-0.01	0.89	0.89	0.41	0.21	0.36				
Pb	0.27	0.54	0.21	0.21	0.52	0.48	0.51	0.24			
Se	-0.10	0.05	0.29	0.47	0.28	0.60	0.51	0.33	0.42		
Zn	-0.10	0.48	0.40	0.30	0.51	0.42	0.10	0.29	0.28	0.17	

<sup>1</sup> Correlation coefficients  $\geq 0.19$  are significant at  $P \leq 0.01$ ; values  $\geq 0.14$  are significant at  $P \leq 0.05$ .

<sup>2</sup> For Hg, values  $\geq 0.22$  are significant at  $P \leq 0.01$ ; values  $\geq 0.17$  are significant at  $P \leq 0.05$ .

## DISCUSSION

### Comparisons with other reported data

The concentrations of heavy metals found in these Queensland soils subjected to normal horticultural practices were all within the typical concentration ranges reported by Alloway (1990) for world-wide agricultural soils (Table 1). However, they exceeded what he terms the 'common value' for some metals. To put these heavy metal concentrations in context with other overseas and Australian reported data, their mean and median concentrations in surface (0-10 cm) soils are presented in Table 7, together with comparative data for (a) soils world-wide (Ure and Berrow 1982), (b) Australian rural surface soils (Tiller 1992) and (c) a recent Queensland survey of surface (0-15 cm) soils (Olszowy *et al.* 1993). When compared to world-wide mean values published by Ure and Berrow (1982), the mean concentrations of Co, Cr, Cu, Ni and Zn found in these Queensland soils are considerably higher, while As, Cd, Hg, Mo, Pb and Se are either lower or of similar value. In particular, excluding Mt. Isa data, Cd concentrations in surface soils ranged from 0.01 to 0.75 mg Cd/kg with arithmetic mean and median values of 0.171 and 0.125 mg Cd/kg respectively. These were considerably lower than Cd data reported in overseas studies (Davies and Paveley 1985; Wiersma *et al.* 1986; McGrath and Loveland 1991; Holmgren *et al.* 1993) where Cd median concentrations ranged from 0.2 - 0.7 mg Cd/kg. Higher background concentrations of Co, Cr, Cu, Ni and Zn in Australian agricultural surface soils relative to their levels in overseas soils, was also noted by Tiller (1992).

**Table 7** Comparative overseas and other Australian heavy metal data and current soil quality guidelines with mean and median concentrations<sup>1</sup> for surface soils (0-10 cm) from this study.

Metal	Median	Mean	Ure and Berrow <sup>2</sup> (1982)	Tiller (1992)	Olszowy <i>et al.</i> (1993)	ANZECC investigation threshold levels <sup>3</sup>
	This Study					
As	2	3	11	<1 - 8	5	20
Cd	0.125	0.195	0.62	<1	0.25	3
Co	26	37	12	<2 - 170		
Cr	65	132	84	5 - 110	6	50
Cu	38	43	26	1 - 190	9	60
Hg	0.035	0.042	0.098		0.05	1
Mo	1.01	1.34	1.9	<1 - 20		
Ni	27	88	34	2 - 400	5	60
Pb	24	27	29	2 - 160	12	300
Se	0.28	0.37	0.40			
Zn	73	76	60	<2 - 200	13	200

<sup>1</sup> n = 191, except for Hg where n = 133

<sup>2</sup> world-wide overall mean values

<sup>3</sup> ANZECC/NHMRC (1992)

Results from this study are comparable to other published heavy metal data on Australian agricultural soils, although in many cases again at the higher end of what is only limited available information (Table 7, Tiller 1992). In particular, Cr concentrations in a number of these horticultural soils were five times the highest background levels reported by Tiller (1992), while Co, Cu, Ni, Pb and Zn were also at or above these levels. Merry *et al.* (1983) reported mean Cu and Pb concentrations in 84 "uncontaminated" agricultural soils of south-eastern Australia of 13 and 15 mg/kg respectively, while 15 surface soils from South Australia contained a mean As concentration of 3.9 mg/kg. Merry and Tiller (1991) found mean EDTA extractable Cd and Pb concentrations in 516 pasture soils from South Australia of 0.18 and 12 mg/kg respectively while McLaughlin (1996) reported a mean EDTA extractable Cd concentration of 0.136 mg/kg for 358 agricultural topsoils (0-15 cm) selected from all States of Australia. However, in a Victorian study of 82 topsoils, McKenzie (1966) reported a mean Mo concentration of 2.98 mg/kg which was considerably higher than the mean value of 1.34 mg/kg found in this study.

The separation of natural concentrations of heavy metals from anomalies imposed by anthropogenic inputs to soils involves defining some relevant baseline or background as a reference and this is difficult to achieve as evidenced by the limited information available in this regard for non-agricultural Australian soils. Some indication of natural or background heavy metal concentrations in soils can be assessed from a recent study by Olszowy *et al.* (1993). This study included a Queensland survey of 120 surface (0-15 cm) soils from National Parks, forests and bushlands believed to be uncontaminated by human activity. The geometric mean values for Cr, Cu, Ni, Pb and Zn found in these soils (Table 7) were considerably lower than median concentrations found in the horticultural soils for the corresponding elements. However, the rural soils selected in the Olszowy *et al.* (1993) study came from only two soil groups (Pullenvale and Beenleigh) which are light textured and generally expected to contain low concentrations of heavy metals (Alloway 1990). Therefore their results may not be a true reflection of the present status of natural background concentrations of heavy metals across the varied soil types found in Queensland. Furthermore, the analytical methods used by Olszowy *et al.* (1993) for Cd and Hg had high detection limits which led to most samples being below reporting limits for these elements. Consequently there is little Queensland data available for these metals for comparative purposes.

There are, however, preliminary data from a study currently underway to examine heavy metal concentrations in Queensland canelands (Rayment *et al.* 1997) which provide some opportunity to compare contemporary concentrations of metals, such as Cd and Hg, in Queensland soils. This study found that mean Cd concentrations in surface soils (0-25 cm) from sites in southern and central Queensland with 10 or more years of cropping history increased four-fold from a background concentration of 0.01 mg/kg in 'paired' uncropped sites. On the other hand, Hg increased almost three-fold from a background concentration of 0.024 mg/kg. While these data are related to different soil types and cropping systems, as well as different surface soil depth of 0-25 cm, there is the indication that Cd could have accumulated at a greater rate in horticultural soils of Queensland compared to those in soils from sugar cane areas, if a similar background Cd concentration is assumed. However, it is clear that mean Cd concentrations in Queensland horticultural surface soils sampled to 2 depths of 0-10 and 10-20 cm (0.195 and 0.167 mg/kg respectively) are considerably higher than those found in caneland soils (0-25 cm) from southern and central Queensland (0.06 mg/kg).

Apart from the work by Barry and Rayment (1992) who found quite high concentrations of Cd in surface 'soils' of Raine Island, the only other reported Cd data for Queensland soils was by Rayment (1994) and McLaughlin (1996). Rayment (1994) evaluated four empirical soil-extractable Cd tests as indicators of soil Cd bio-availability on these same horticultural soils and found the highest mean Cd levels ( $\pm$  standard deviation) in the surface (0-10 cm) were  $0.188 \pm 0.180$  mg/kg (air-dry basis). This mean Cd value, based on a 1.0 M HCl extraction, is only slightly less than the  $0.195 \pm 0.238$  found by the HNO<sub>3</sub>/HCl method employed in this study. McLaughlin (1996) reported a mean EDTA extractable Cd concentration of 0.109 mg/kg for 63 Queensland agricultural topsoils (0-15 cm).

There appears to be no published information on Hg concentrations in Australian agricultural soils. The median and arithmetic mean values of 0.035 and 0.042 mg Hg/kg respectively for 133 Queensland horticultural surface soils represent the first significant reporting of Hg concentrations in Australian horticultural soils. By world standards, these values lie at the bottom end of the range reported for 'uncontaminated' soils with an overall mean listed by Ure and Berrow (1982) as 0.098 mg/kg for over 3000 soils from a wide range of countries. This suggests that Hg contribution from anthropogenic sources to these Queensland soils is relatively small. In addition, their mean Hg concentrations ( $0.042 \pm 0.03$  mg/kg) are considerably lower than those reported by Rayment *et al.* (1997) for Queensland canelands ( $0.076 \pm 0.058$  mg/kg).

The median Mo concentration of 1.01 mg/kg is quite low compared to values found by Giles (1959). He reported a median Mo concentration of 7.1 mg/kg for 118 Queensland surface soils from a range of soil groups across the State which included, interestingly, Black Earths from the Darling Downs and Krasnozems from Toowoomba - both areas and soil types from which soils were sampled in this current study.

### Regional differences and metal relationships

There were wide differences in the regional distribution of some heavy metals in these horticultural soils throughout Queensland as evidenced by the median concentrations presented in Table 4. Likely reasons for these differences are: (a) natural pedogenic processes on different parent rock materials (b) anthropogenic inputs from fertilisers, pesticides, waste materials etc. and (c) natural mineralisation and/or atmospheric deposition. While the data from Mt.Isa are limited, highest median concentrations of Cd, Cu, Hg, Pb and Zn were found in these soils, reflecting both their natural mineralised status of these metals and the possible impact from atmospheric deposition as a consequence of mining activity.

Good evidence of the effect of geological and soil forming factors on soil heavy metal concentrations can be seen in the patterns of heavy metal distribution illustrated in Figure 2 and when the elements are grouped according to the geochemical classification by Goldschmidt (Alloway 1990). For example, similar patterns of the relative order of decreasing median concentrations in surface soils across districts were shown by siderophile (iron-loving) elements Co, Cr and Ni. For each of these metals, their median concentrations ranged from highest in surface soils from the Mareeba/Atherton region to lowest in soils from the Granite Belt area. Moreover, further support for the strong relationships between these metals is shown by their positive and significant ( $P < 0.01$ ) correlation coefficients in Table 5.

Other heavy metals such as Cd, Cu, Hg, Pb, Se and Zn, which are classified as chalcophile elements (sulphur-loving), all had positive and significant ( $P < 0.01$ ) correlation coefficients between them (Table 5). This geochemical grouping may explain, for example, the reason for the highest median concentrations of both Hg (excluding Mt.Isa district) and Se occurring in soils from the Bundaberg/ Gympie region. There is also a strong geochemical link between Mo and Se in many soils (Ure and Berrow 1982). Interestingly, the Mo/Se ratios for median surface soil concentrations across districts were in the range 2.5-5.4, except for the Granite Belt region where it was 12.2. This abnormally higher ratio indicates an enrichment of Mo relative to Se and suggests either cultural practices or a natural aberration are responsible. Furthermore, sandy or siliceous soils have lower Mo concentrations than clay soils and generally subsoils tend to be richer in Mo than surface horizons (Ure and Berrow 1982). The

siliceous sands sampled in the Granite Belt region had the lowest mean clay content (0-10 cm) of 9% compared to the soils from Lockyer/Fassifern/Toowoomba with 46%, yet contained Mo at concentrations higher than expected, being similar to those from Lockyer/Fassifern/Toowoomba areas. Moreover, for six sites in the Granite Belt where depth comparisons could be made, the median Mo concentration for 0-10 cm depth segments (1.15 mg/kg) was considerably higher than for the corresponding 20-30 cm depths (0.78 mg/kg), and this higher concentration of metals in surface soils can indicate inputs from anthropogenic origin (Kabata-Pendias 1991), although it is understood Mo was mined in the area some years ago. It is also noteworthy that Mo was at elevated concentrations in the edible portions of several vegetables grown in this region relative to concentrations in the same vegetable species from other districts (Rayment 1994 a).

Apart from the Mt. Isa area, the highest median Cd concentration was found in surface soils from the Brisbane/Caboolture/Redlands areas (0.184 mg/kg) with the lowest in soils from Ayr/Bowen (0.082 mg/kg). Over all areas (excluding Mt. Isa) there was a positive correlation ( $r = 0.59$ ,  $P < 0.01$ ;  $n = 185$ ) between total P and total Cd in surface soils indicating that the use of P fertilisers has played a significant role in the Cd enrichment of these horticultural soils of Queensland. Relationships between soil Cd and P have been shown by other workers both for soils from this survey (Rayment 1994 a) and for soils elsewhere in Australia and overseas (Merry 1988; McLaughlin 1996; Roberts *et al.* 1996). Between districts however, this relationship varied considerably from highly significant ( $P < 0.01$ ) for Mareeba/Atherton, Lockyer/ Fassifern/Toowoomba, Bundaberg/Gympie and Granite Belt (correlation coefficients of 0.71, 0.72, 0.77 and 0.56 respectively) to a non significant correlation for Brisbane/Caboolture/Redlands (correlation coefficient of 0.17), the area with the highest median Cd concentration.

It is possible that soils from this region are more "urban influenced" than those from other "more rural areas" and as such have other more significant Cd sources contributing to them which mask Cd inputs from P fertilisers e.g. industrial and automotive atmospheric deposition. Evidence for this was supported by further separation of sites within this region which showed median Cd concentrations in surface soils from Brisbane ( $n = 16$ ) and Caboolture/Redlands ( $n = 20$ ) sites were 0.286 and 0.143 mg/kg respectively. Other explanations could be that the soils from the Brisbane area contain higher "natural" P levels or that alternative P fertiliser sources low in Cd have been used since, for the Brisbane sites a negative correlation existed ( $r = -0.36$ ) between soil Cd and P.

Rayment (1994) predicted Cd inputs from P fertilisers into Queensland vegetable soils would increase soil Cd concentrations by at least 0.047 mg/kg in the top 10-15 cm depth. If this is accepted, the median Cd concentrations found in these horticultural soils within each district indicate other sources have contributed to various degrees depending on the initial background levels in the soils. Certainly the 'more urban' soils around Brisbane contain Cd at levels much greater than would be expected solely from P fertilisers than do 'more rural' soils.

A similar trend occurred for Cu, Pb and Zn where their median concentrations in surface soils from Brisbane were higher than those from Caboolture/Redlands again indicating an 'urban' influence on these soil metal levels, which is also in agreement with the findings of Olszowy *et al.* (1993).

While the total Cd concentrations were highest in surface soils around Brisbane, only two samples of silverbeet from a wide range of vegetable types sampled in this region in the Cd bio-availability survey (Rayment 1994), actually exceeded the maximum permissible concentration (MPC) for Cd of 0.05 mg/kg (fresh weight) as listed in the Australian Food Standard Code for the category "foods not containing a food otherwise specified". Indeed, only seven samples, from a total of 191, exceeded this MPC with over 50% being less than half the MPC. There are clear implications here that while knowledge of the 'total' soil content of a metal is important from a pollution view point, an understanding of the soil mechanisms/processes, which determine bio-available metal fractions, is imperative from a food quality consideration.

### Effect of soil depth

While mean Cd, Cu, Pb and Zn concentrations decreased ( $P < 0.005$ ) with increasing depth across all districts (Table 5), Cd was the only heavy metal whose concentrations were significantly higher ( $P < 0.001$ ) in surface (0-10 cm) relative to subsurface depths (20-30 cm) within each district. Although a similar Cd trend occurred between 0-10 cm and 10-20 cm depths, such differences were much smaller and probably due to the cultivation of vegetable growing soils to 20 cm.

The preliminary study by Rayment *et al.* (1997) found an enrichment of Cd (as well as Hg) in surface soils (0-25 cm) relative to subsurface depths (25-50 cm) from southern and central Queensland sugar areas. Merry and Tiller (1991) found the median EDTA extractable Cd concentration in the 0-5 cm depth of over 500 pasture soils was double that for those in the 5-10 cm depth. However, the more significant decrease in Cd concentration at a shallower depth in these soils is an indication of different cultural practices compared to those in horticultural soils. Pierce *et al.* (1982) also found the predominant trend was for higher concentrations of Cd, Pb and Zn in surface soils (0-15 cm) relative to subsoil, as did McLaughlin (1996) for EDTA extractable Cd in a range of Australian potato growing soils.

Many studies have looked at the distribution of heavy metals within the soil profile with Cd, Cu, Pb and Zn generally found to be at higher concentrations in surface horizons partly as a reflection of inputs from atmospheric deposition, fertilisers, cycling through plants and adsorption by soil organic matter (Alloway 1990). Such anthropogenic inputs as well as these other factors probably explain why other heavy metals (as well as Cd) were enriched in surface (0-10 cm) relative to those in sub-surface (20-30 cm) depths in several areas e.g. Cu, Pb and Zn in soils from Brisbane/Caboolture/Redlands and Mt. Isa regions; Cu, Mo, and Zn in soils from the Granite Belt.

In contrast, there was little effect of sampling depth on soil concentrations of Co, Cr, Ni and Se to 30 cm and this is consistent with minimal anthropogenic inputs of these elements and that such concentrations are mainly due to the parent materials from which the soils are derived.

### **Relationships with environmental soil quality guidelines**

There are a number of Australian States developing environmental guidelines for the assessment and management of contaminated sites. In Queensland there is the Contaminated Land Act (1991) while the Australian and New Zealand Environment and Conservation Council (ANZECC) and the National Health and Medical Research Council (NHMRC) jointly developed such guidelines in 1992. The environmental soil quality guidelines listed for heavy metals and other contaminants in both of the above documents are interim guidelines only and depend on continued studies such as this survey to gain further information on their current background concentrations in Australian soils. Based on the current ANZECC/NHMRC (1992) environmental investigation threshold levels for heavy metals (Table 7), a large proportion of the surface soils sampled in this study would exceed their relevant threshold levels. In particular, 66, 40 and 20 percent of samples tested for Cr, Ni and Cu respectively, exceeded the threshold levels currently set for these metals.

While the environmental investigation levels should only be used as a guide in deciding whether a site needs further investigation and that site specific issues also need to be considered, the results from this study indicate that such levels currently set in ANZECC/NHMRC (1992) are somewhat conservative for several heavy metals, particularly Cr, Cu and Ni, and possibly Zn. There is justification therefore to raise the threshold levels to better reflect the normal background heavy metal concentrations that currently exist in Australian agricultural soils.

### **CONCLUSIONS/RECOMMENDATIONS**

This study provides valuable new information on the regional distribution of heavy metal levels in Queensland rural soils, particularly Cd, Co, Hg, Mo and Se. With a better understanding on the extent of existing accumulations of heavy metals in these soils the horticultural industry can adopt appropriate management plans and develop sustainable practices on a more rational basis. Clearly, as more information on contemporary background levels of heavy metals in Australian horticultural soils is forthcoming, the ability to identify any potential environmental or human health risk problems which may arise from past horticultural practices increases.

The results from this study provide a substantial database of information which will not only be of benefit to the Queensland horticultural industry but also to Environmental and Health authorities by providing valuable information to assist them formulate guidelines which set "environmental investigation levels" based on appropriate heavy metal levels in Australian soils.

Heavy metal concentrations found in these Queensland soils were within typical ranges reported in both overseas and Australian studies. However, some metals were at the high end of this range, such as Cu, Co, Cr, Ni and Zn, while Cd and Hg were generally lower. Chromium concentrations were considerably higher than reported elsewhere for Australian soils. There were wide regional variations in soil concentrations throughout Queensland which were attributed to a number of reasons. For example, there was good evidence for pedogenic processes being responsible for the wide range of Co, Cr and Ni concentrations,

while soils from Mt. Isa were influenced by the natural mineralisation and possible atmospheric deposition.

A positive and highly significant correlation between total P and Cd in many regions implicated the use of P fertilisers as a significant source of Cd input to these horticultural soils. However, there was no such correlation for soils sampled around the Brisbane area.

While the Cd concentrations in these horticultural soils were within typical ranges reported in other Australian studies, they were considerably higher than those found in southern and central Queensland canelands. Whether this is due to a greater accumulation rate of Cd in soil from fertilisers and other external inputs or to a higher initial soil background concentration needs further investigation.

The results confirm the findings of other Australian workers that the current environmental investigation levels for some heavy metals, such as Cr, Cu, Ni and possibly Zn, are too conservative with many of these horticultural soils being "naturally" above the threshold levels.

**Based on the findings of this study, the following RECOMMENDATIONS are made:**

- A more detailed survey of potential Cd sources to vegetable soils of the Brisbane region be undertaken to clarify reasons for the lack of correlation between total soil P and soil Cd, with the objective of identifying (and subsequently minimising) alternative sources of contamination;
- A detailed survey of 'paired' cropped and uncropped (minimal impact from human activity) sites, particularly from areas at the high end of the soil Cd, Cu and Zn concentration ranges, be undertaken to better understand the impact of cropping from past horticultural practices on the "more natural" baseline soil heavy metal concentrations.
- A detailed survey of the heavy metal status of vegetable growing areas of the Mt. Isa and other known mineralised areas be undertaken as a matter of urgency, the study to include a wider selection of soils, vegetables and bio-availability indices.
- Studies on the relationships between soil and vegetable Cd concentrations be investigated as a means of determining how potentially high risk soils (high Cd concentrations) can best be utilised by appropriate management strategies by the grower.
- The horticultural soils of Queensland, mostly from the same locations, be re-sampled approximately seven years from the initial sampling to delineate condition and trend from a resource sustainability viewpoint.
- Further detailed surveys of the heavy metal status of Australian horticultural soils should be undertaken to build on the information database from this Queensland study so as to provide regulatory authorities with more relevant information on which to formulate appropriate 'environmental investigation threshold' levels.

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**Appendix 1 Methods of analysis for determining heavy metals in soils**

Element	Digestion/extraction procedure	Analytical finish <sup>a</sup>
Co, Cu, Cr, Ni, Pb and Zn	pellet/pressed powder with boric acid technique	XRF
As, Se	nitric:perchloric:sulphuric acid (13:1:2) digest	hydride AAS
Cd	nitric:hydrochloric acid (6:2) extraction on steam bath for 2 hr	GFAAS
Hg	nitric:hydrochloric acid (6:2) extraction on steam bath for 2 hr	cold vapour AAS
Mo	nitric:perchloric:sulphuric acid (13:1:2) digest	ICPMS

<sup>a</sup> ICPMS = inductively coupled plasma mass spectrometry; GFAAS = graphite furnace atomic absorption spectrometry; XRF = x-ray fluorescence spectrometry.

**Appendix 2 Lower limits of reporting (mg/kg) for heavy metals analysed in this study**

As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
0.6	0.01	6	9	8	0.006	0.05	10	4	0.05	12