Heavy metals contamination of home grown vegetables near metal smelters in NSW.

Anthony Kachenko and Balwant Singh

Faculty of Agriculture, Food and Natural Resources, The University of Sydney, NSW 2006, Australia. Email akac1808@mail.usyd.edu.au

Abstract
Industrial activities such as smelters are a leading cause of metal emissions, often associated with elevated soil and plant metal concentrations in adjacent regions. The accumulation of Cd, Cu, Pb and Zn in soils and vegetables in the vicinity of 2 industrial regions, Port Kembla and Boolaroo, were investigated. Soil samples (*n*=37) were collected at depths of 0-30 and 60-90 cm, air dried and sieved to obtain <2mm fraction. Soil properties including pH, EC, organic carbon, total cation exchange capacity and total metal content were determined. Vegetable samples (*n*=40) predominantly leafy, included - lettuce, spinach, leek, mint and parsley. The plant samples were oven dried and analysed for total metal content. Soil metal concentrations decreased with depth at the two sites, suggesting anthropogenic sources of contamination. The soils at Boolaroo contained the highest levels of Cd, Pb and Zn. Vegetable samples collected from Boolaroo recorded very high levels of Cd and Pb, and ≥ 95% of the samples had Cd and Pb levels exceeding the maximum level (ML) set by the Australian and New Zealand Food Authority (i.e. both Cd and Pb MLs are 0.01 mg kg^{-1} fresh weight). At Port Kembla 17% of the vegetable samples exceeded the ML of Cd and 44 % exceeded the ML of Pb. Correlation analysis identified a strong relationship between soil and vegetable Cu concentrations, and was strengthened by the determination of transfer coefficients. The results of this study suggest that vegetables grown in the vicinity of industrial sites are subject to atmospheric deposition of heavy metals and pose a risk to humans if consumed.

Key Words
Trace metals, pollution, bioavailability, uptake, guidelines, source

Introduction
Several studies have indicated that vegetables, particularly leafy crops, grown in heavy metals contaminated soils have higher concentrations of heavy metals than those grown in uncontaminated soil (Guttormsen *et al*. 1995; Dowdy and Larson 1995). A major pathway of soil contamination is through atmospheric deposition of heavy metals from point sources such as: metaliferous mining, smelting and industrial activities. Other non point sources of contamination affecting predominantly agricultural soils include inputs such as, fertilisers, pesticides, sewage sludge, organic manures and composts (Singh 2001). Additionally, foliar uptake of atmospheric heavy metals emissions has also been identified as an important pathway of heavy metal contamination in vegetable crops (Bassuk 1986; Salim *et al*. 1992). Vegetable growing areas are often situated in, or near sources of atmospheric deposits, and thus have an elevated risk of potential contamination. There are two distinct regions in New South Wales where there is heavy industrial activity located in an otherwise non-industrial, residential region: Port Kembla and Boolaroo.

The region of Port Kembla is situated on an artificial harbour, 80 km south of Sydney, New South Wales Australia. It is a major industrial port where heavy industry including a Cu smelter (which has operated sporadically in the last decade), steelworks and fertilizer plant are located. Past studies have identified widespread heavy metals contamination in the Port Kembla Harbor marine environment (Moran 1984; He and Morrision 2001). Studies have also identified heavy metals contaminated soils in the vicinity of the Port Kembla industries, and have identified the smelter as the principle source of contamination (Beavington 1973; Martley *et al*. 2003).

The region of Boolaroo is located 15 km southwest of Newcastle, NSW and is host to a Pb and Zn smelter located centrally within the region. The smelter had been in operation since 1897, ceasing operations in September 2003. A fertiliser plant occurs adjoining the smelter. A number of studies have reported heavy metal contamination in soils and plants of the areas surrounding the smelter (Galvin *et al*. 1992; Tam and Singh 2004).

There have been a number of studies which have investigated atmospheric deposition of heavy metals in soil and/or vegetables growing in the vicinity of industrial areas (Gzyl 1995; Voutsa *et al*. 1996). These studies indicate high concentrations of heavy metals in vegetables grown in the vicinity of industries and identify leafy vegetables at greatest risk of accumulating elevated concentrations. There is, however, limited published information on contamination of vegetables grown in the vicinity of Australian industrial areas. In Australia, the National Environmental Protection (Assessment of Site Contamination) Measures (NEPM 1999) identifies environmental investigation levels (EIL) which define threshold values of certain heavy metals in soils. Maximum levels (ML) also exist for Cd and Pb in vegetable crops (fresh weight basis), and are applied by the Australian and New Zealand Food Authority (ANZFA) (Anonymous 2001).

This paper reports Cd, Cu, Pb and Zn levels in soils and vegetables from residential properties located near a Cu smelter in Port Kembla and a Pb-Zn smelter in Boolaroo. The aim was to highlight the contamination status of vegetables grown on smelter polluted soils, and to identify the interactions between soil and vegetable metal concentrations.

Methods

Sampling

A total of 37 soil samples and 40 plant samples were collected from the two regions in April 2003. A total of 16 sites were sampled, 11 in Boolaroo and 5 in Port Kembla. At each sites a transect of 5 m × 5 m was selected at random from which both soil and vegetable samples were collected. From each transect two composite soil samples were collected at 0-30 cm (n= 21) and at 60-90 cm (n=17) depths. At Port Kembla 2 transects were selected at each site, however only one 60-90 cm sample was collected. Each composite soil sample comprised of 5 subsamples taken at random locations within the transect.

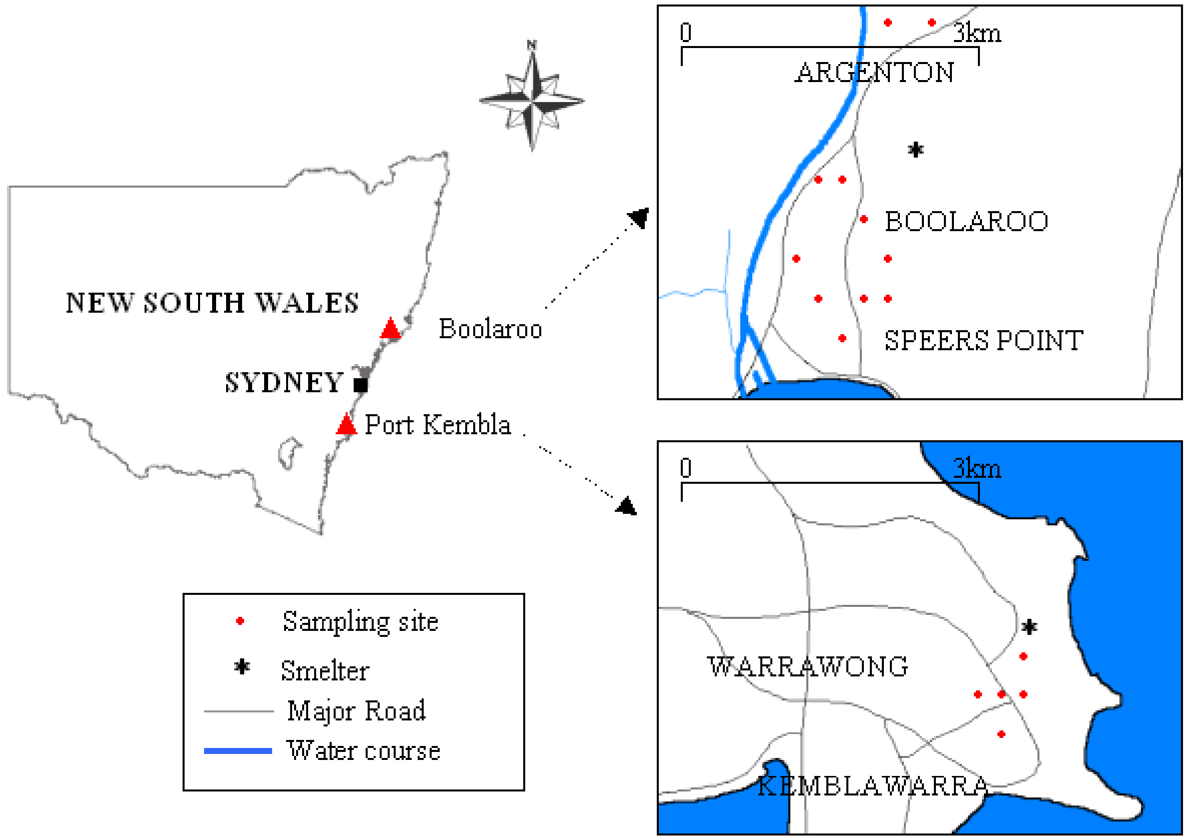

Fig.1. Location of sampling sites

The edible portions of 2 plants (e.g. leafy, herb or stem depending on types grown at each site) were randomly sampled from each transect. Leafy vegetables were preferred for sampling since past research indicates that they accumulate heavy metals at a greater capacity than other vegetables (Jinadasa *et al*. 1997). The number of plant samples collected from Boolaroo and Port Kembla were 22 and 18 respectively. The vegetables sampled included 12 lettuce (*Lactuca sativa* L.), 16 spinach (*Spinacia* *oleracea* L.), 4 leek (*Allium porrum* L.), 4 parsley (*Petroselinum crispum* var. *crispum***)** and 4 mint (*Mentha spicata* L.).

Soil analysis
The soil samples were air-dried, mechanically ground and sieved to obtain <2 mm fraction. A 20-30 g subsample was drawn from the bulk soil (<2 mm fraction) and reground to obtain <200 μm fraction using a mortar and pestle. This fine material was used to determine organic carbon, cation exchange capacity (CEC) and total metal content of soil. The <2 mm fraction was used to determine pH (1:5 soil water extract), electrical conductivity (EC) (1:5 soil water extract) and particle size analysis using standard laboratory methods (Rayment and Higginson, 1992). Organic carbon was determined by the modified Walkley and Black method (McCleod 1973); cation exchange capacity by the silver thiourea method (Rayment and Higginson 1992). Soil samples were digested according to the USEPA Method 3050B (USEPA 1996) for the analysis of heavy metals (Cd, Cu, Ni, Pb and Zn). The extracts were analysed using a Vista Varian inductively coupled plasma atomic emission spectrometer (ICP-AES). A graphite atomic absorption spectrophotomer (Vista Varian Spectra 220Z) was used to measure concentrations of Cd < 1 mg/kg $^{-1}$ in soil extracts.

Plant analysis
The plant samples were put through a three step washing sequence (Reuter *et al.* 1983), air dried, weighed and placed in a dehydrator at approximately 80°C for 48-72 hours depending on sample size. Dried samples were weighed and mechanically ground (<1 mm) for acid digestion (Miller 1998). Similar to with soil samples, plant digests were analysed for various elements using ICP-AES and Cd using a graphite atomic absorption spectrophotomer (Vista Varian Spectra 220Z).

Statistical analysis was performed by using Genstat version 6.1.0.234 (Payne 2002). Soil and plant data were not normally distributed and were log transformed prior to statistical analysis. Statistically significant differences were determined using residual maximum likelihood (REML) regression analysis.

Results

General soil properties
The soils had a wide range of values for measured properties (Table 1). Soil pH values in water varied from mildly acidic (pH 5.60) to moderately alkaline (pH 7.52) and varied little with depth. Electrical conductivity values ranged form 71 μS cm $^{-1}$ to 896 μS cm $^{-1}$ and suggest non-saline growing conditions in the studied regions. Topsoils generally had higher organic carbon (%) than subsoils, however clay content (%) decreased with depth. Cation exchange capacity values were generally low across regions and levels were similar between layers. Free Fe content (%) was greatest at Port Kembla, and increased with depth in the sampled soils.

The distribution of Cd, Pb, Cu and Zn in soil profiles
At Boolaroo and Port Kembla, heavy metals concentrations decreased significantly (P<0.05) with depth (Fig. 1) suggesting anthropogenic sources of contamination. Contamination was more apparent in soils at Boolaroo where Cd, Pb and Zn levels were highest (P<0.05). At Boolaroo Cd concentrations ranged from 0.01 mg kg $^{-1}$ (subsoil) to 28 mg kg $^{-1}$ (topsoil). Soil Pb and Zn concentrations showed a trend similar to soil Cd. Lead concentrations in soils at Boolaroo ranged from 12 (subsoil) to 1626 (topsoil) mg kg $^{-1}$ and the mean topsoil and subsoil Pb concentrations were 363 and 64 mg kg $^{-1}$, respectively. These levels were higher than those reported by Merry and Tiller (1978) in soils near the vicinity of a Pb and Zn smelter in Port Pirie, South Australia (0.12-258 mg kg $^{-1}$). The samples analysed by Merry and Tiller (1978) were located >2km from the site of the smelter and were found to decrease with distance, whereas the majority of samples in this study were within a 2km radius of the smelter. Zinc concentrations in soils at Boolaroo ranged from 45 (subsoil) to 4014 mg kg $^{-1}$ (topsoil) and the mean concentrations for topsoils and subsoils were 1062 and 291 mg kg $^{-1}$, respectively. The concentrations of Cd, Pb and Zn in soils at Boolaroo correspond to a study by Tam and Singh (2004) who reported similar Cd (0.03-55 mg kg $^{-1}$), Pb (20 to 3609 mg kg $^{-1}$) and Zn (20 to 2613 mg kg $^{-1}$) concentrations in soils from within the smelter compound in Boolaroo.

The highest Cu concentrations were observed in topsoils from the Port Kembla region (Fig. 1b), with a mean concentration of 338 mg kg $^{-1}$. Similar levels were found by Beavington (1973) who reported elevated soil Cu concentrations (mean value of 343 mg kg $^{-1}$) that decreased with depth in a 1 km radius surrounding the smelting plant in Port Kembla smelter. These results indicate the smelter is still of concern in relation to Cu emissions, however the level of Cu contamination appears to have remained static over the past 30 years. Similarly Gundermann and Hutchinson (1995) found elevated levels of Cu within a 2 km radius of a Ni-Cu smelter in North America, with levels decreasing at distance from the smelter. In Port Kembla samples, Cd concentrations ranged from 0.01-7.01 mg kg $^{-1}$, Pb concentrations ranged from 13.9-430 mg kg $^{-1}$ and Zn concentrations ranged from 86-1947 mg kg $^{-1}$.

Table 1. Chemical and physical properties of the studied soils.

Soil property		Boolaroo		Port Kembla	
		Topsoil (0-30 cm)	Subsoil (60-90 cm)	Topsoil (0-30 cm)	Subsoil (60-90 cm)
pH (1:5 H_2O)	Mean±SD	6.49±0.42	6.42±0.59	6.65±0.49	6.99±0.56
	Median	6.44	6.27	6.58	7.14
	Range	5.65-7.12	5.60-7.27	5.99-7.26	6.07-7.52
EC µS cm $^{-1}$	Mean±SD	265±125	108±37	340±167	325±282
	Median	255	100	262	219
	Range	191-626	71-186	141-667	159-896
Organic Carbon (%)	Mean±SD	3.6±1.4	1.2±1.06	3.4±1.20	1.0±0.61
	Median	2.9	0.9	3.0	0.8
	Range	2.2-6.3	0.1-3.2	1.6-5.8	0.6-2.2
Clay (%)	Mean±SD	12.1±3.59	30.3±21.3	16.0±7.9	34.2±17.3
	Median	12.0	17.7	15.4	42.2
	Range	8.0-17.9	9.9-63.9	6.9-30.0	5.0-49.5
CEC (mmol$_c$ kg^{-1})	Mean±SD	129±31	101±53	155±29	156±59
	Median	121.21	91.58	160.90	176.59
	Range	84.75-180.78	40.99-185.83	98.02-196.33	42.01-203.57
Free Fe content (%)	Mean±SD	1.55±0.48	1.72±0.85	3.83±1.60	5.48±2.28
	Median	1.52	1.76	3.80	6.36
	Range	0.845-2.53	0.55-2.94	1.68-5.93	1.26-7.26

Heavy metals in vegetables

Cadmium, Cu, Pb and Zn concentration in vegetables sampled (Fig. 2) followed a trend similar to soil heavy metals concentrations (Fig. 1). Cadmium, Pb and Zn concentrations were highest in vegetables at Boolaroo. Cadmium levels ranged from 1.34 to 14.5 mg kg $^{-1}$ dry weight (DW). The mean Cd concentration in broad leaf samples was 4.03, herbs 9.53 and stems 1.51 mg kg $^{-1}$ DW. Zinc levels were greatest in leafy vegetable and herbs, with a mean of 738 and 414 mg kg $^{-1}$ DW respectively. A study by Davies and White (1981) reported similar Cd (<0.05 to 43 mg kg $^{-1}$ DW) and Zn (39.0 to 710 mg kg $^{-1}$ DW) concentrations in vegetables grown on soils contaminated by base metal mining. At Boolaroo Pb concentrations ranged from 16.8 and 375 mg kg $^{-1}$. The mean concentrations in broad leaf vegetables were 54 mg kg $^{-1}$, herbs 228 mg kg $^{-1}$ and stems 20 mg kg $^{-1}$ DW.

Copper concentrations were greatest in the vegetables sampled at Port Kembla, and ranged from 9.6-245, with a median of 31.4 mg kg $^{-1}$ DW. These levels are similar to Cu concentrations observed in vegetables by Vousta *et al*. (1996) grown near an industrial area in Greece (17.9 - 39.5 mg kg $^{-1}$, with a median value of 26.8 mg kg $^{-1}$ DW). Beavington (1975) reported a mean Cu concentration of 23 mg kg $^{-1}$ in lettuce grown in the vicinity of the smelter complex at Port Kembla, which is similar to the Cu concentration of the lettuce sampled in this study (27.6 mg kg $^{-1}$ DW). In the vegetables sampled from Port Kembla, Cd concentrations ranged from 0.20-1.35 mg kg $^{-1}$ DW, Pb concentrations ranged from 0.02-6.13 mg kg $^{-1}$ DW and Zn concentrations ranged from 47-350 mg kg $^{-1}$ DW.

Discussion

Soil contamination was evident in both regions, and corresponds closely to the differences in emissions as a result of the smelting processes. Cadmium concentration in most soils from Boolaroo and Port Kembla were greater than the reported range for Australian soils (0.032-0.21 mg kg $^{-1}$) (Williams and David, 1973), and the normal range (0.001-0.7 mg kg $^{-1}$) reported for the worlds soils (Ure and Berrow 1982). Fifty percent of the soils sampled at Boolaroo and 32 % of those from Port Kembla exceeded the 3 mg kg $^{-1}$ environmental investigation level (EIL) for Cd (NEPM 1999). These levels reflect Cd smelter emissions during the year 2002-2003 indicating greater Cd emissions in Boolaroo (530 kg) than in Port Kembla

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(150 kg) (NPI 2004). Similarly the level of soil Cu contamination in both regions reflects the degree of emissions from both smelters. In Port Kembla during 2002-2003, 2200 kg of Cu and compounds were emitted from the smelter with three quarters of the soils sampled exceeding the NEPM (1999) EIL for Cu (100 mg kg $^{-1}$). However, in Boolaroo 140 kg of Cu and compounds were emitted during 2002-2003 with only 23% of soils sampled exceeding this guideline value (NPI 2004). Concentrations of Pb in soils were high in both regions, however, only 3 samples investigated from Boolaroo exceeded the 600 mg kg $^{-1}$ EIL (NEPM 1999). The reported range of Zn for Australian soils (11-86 mg kg $^{-1}$) was exceeded in 97% of soils from Boolaroo and Port Kembla regions combined (McKenzie 1960). The NEPM (1999) EIL for Zn (200 mg kg $^{-1}$) was exceeded in 73% and 69 % of the samples from Boolaroo and Port Kembla, respectively. As with Cd and Cu, the degree of Zn contamination in soils sampled reflects the degree of emissions from both smelters. In Boolaroo during 2002-2003, 17 000 kg of Zn and compounds were emitted from the smelter, more than 4 times the level of emissions recorded in Port Kembla (4200 kg).

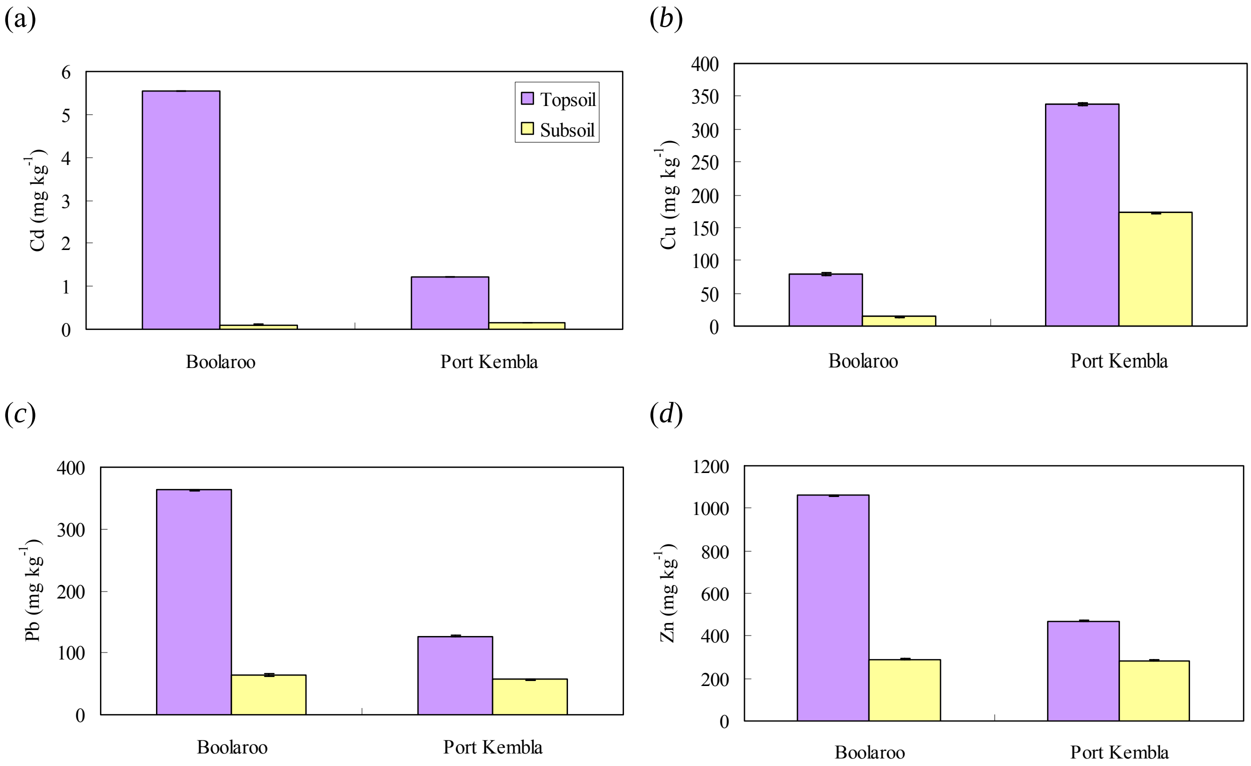

Fig. 1. Regional least square means (mg kg $^{-1}$) of (a) cadmium, (b) copper, (c) lead and (d) zinc for topsoil (0-30 cm) and subsoil (60-90 cm) layers. The magnitude of the standard error for the least square means are indicated by the error bars.

Broad leaf vegetables and herbs accumulated greater concentrations of most heavy metals. Ninety five percent of the vegetables sampled from Boolaroo exceeded the ANZFA 0.1 mg kg $^{-1}$ fresh weight ML for Cd allowable in vegetable crops (Anonymous 2001). The high accumulation of Cd in plants at Boolaroo may be attributed to the acidic nature of the soil (Table 1), resulting in greater Cd availability (Singh 2001), or the uptake of aerial deposited Cd by vegetable leaves. At Port Kembla, 19% of vegetables exceeded the ANZFA ML for Cd. A moderate correlation was observed between vegetable Cd and soil Cd (r = 0.66), soil Zn (r = 0.69) and plant Zn (r = 0.77). These findings suggest interaction between Cd and Zn in both vegetables and soils are important, and corroborate with the results of McKenna et al. (1993) in relation to the known geochemical association between the two metals. Jinadasa et al. (1997) also identified an interaction between soil Cd and Zn (r = 0.51 P<0.05) in soils from the Sydney basin.

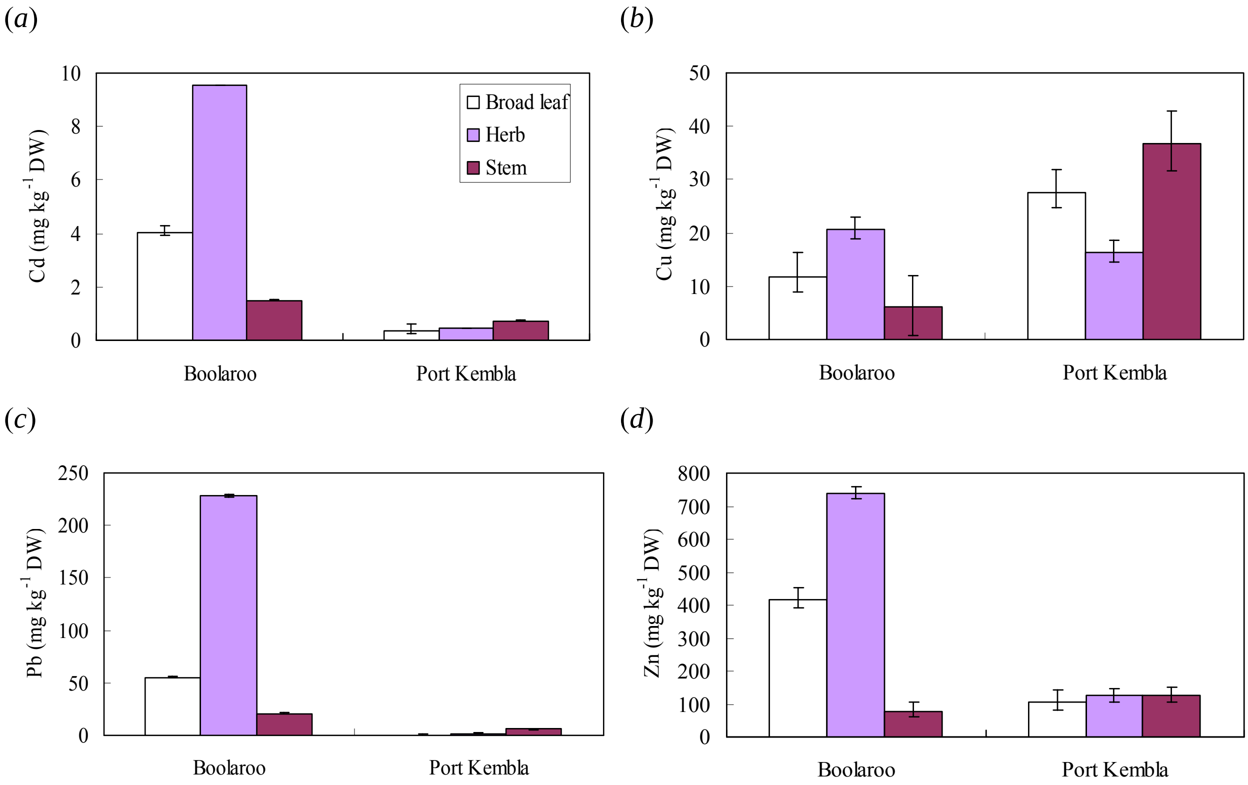

Fig. 2. Regional least squared means (mg kg $^{-1}$ dry weight) of (a) cadmium, (b) copper, (c) lead and (d) zinc for three vegetable categories. The magnitude of the standard error for the least square means are indicated by the error bars.

Lead levels were greatest in vegetables grown in Boolaroo. All samples from Boolaroo exceeded the ANZFA ML for Pb allowable in vegetable crops (0.3 mg kg $^{-1}$ FW for brassicas and 0.1 mg kg $^{-1}$ FW for all remaining vegetables). Lead levels at Port Kembla ranged from 0.02 to 6.13 mg kg $^{-1}$ DW, with 60 % of the samples exceeding the ANZFA ML for Pb. A moderate degree of correlation was observed between plant Pb and soil Pb ($r = 0.68$). Lead is not readily translocatd from roots to shoots (Kabata-Pendias and Pendias 1992) and the high levels observed in vegetables may be a result of aerial deposition of Pb. During 2002-2003, 11 000 kg of Pb and compounds was emitted from the smelter in Boolaroo and 1300 kg from the smelter in Port Kembla (NPI 2004).

At present there are no guidelines to enforce the ML of Zn and Cu in vegetables, thus the extent of Zn and Cu contamination was not addressed. A marked degree of correlation was observed between vegetable Cu and soil Cu ($r = 0.75$) and a moderate degree of correlation occurred between vegetable Zn and soil Zn n ($r = 0.59$). The soil metal concentrations appear to influence the uptake of Cu and to a lesser extent Zn.

Transfer coefficients were determined for all metals to quantify the relative differences in bioavailability of metals to plants or to identify the efficiency of a plant species to accumulate a given metal. The transfer coefficients as suggested by Kloke *et al*. (1984) for Cu and Pb (0.01-0.1), and Cd and Zn (1-10) were used as a generalised range for comparison. These coefficients were based on the root uptake of metals and discount the foliar absorption of atmospheric metal deposits. No samples exceeded the Cd and Zn suggested coefficient range as suggested by Kloke *et al.* (1984). At Boolaroo, 82% of samples exceeded the suggested coefficient range of Cu, and 63% exceeded the suggested Pb coefficient range. At Port Kembla, 5 % of samples exceeded the suggested coefficient range of Cu. The high number of samples exceeding the suggested coefficient range of Pb and Cu at Boolaroo and Port Kembla reflect the elevated topsoil metal concentrations found at these regions. Soil properties may have further influenced the soil-plant transfer of Cu and Pb. The acidic nature of the topsoils from Boolaroo and Port Kembla (Table 1) may have increased availability of metals for vegetable uptake. Furthermore, the low Organic Carbon contents (Table 1) of soils sampled could have also enhanced soil-plant transfer of metals.

Conclusions

The high levels of soil contamination in the regions of Boolaroo and Port Kembla appear as a result of anthropogenic activities, with smelters in both regions the likely contributor. The degree of soil contamination related closely with the emissions released from the smelters during the duration of sampling and furthermore, all metals decreased in concentration between topsoil and subsoil layers. The topsoils sampled from Boolaroo were contaminated the most, containing the highest mean concentrations of Cd (5.5 mg kg $^{-1}$), Pb (364 mg kg $^{-1}$) and Zn (1061 mg kg $^{-1}$). Similarly, topsoils sampled from Port Kembla were contaminated the most with Cu (83-1032 mg kg $^{-1}$), and had high concentrations of Zn (192-1641 mg kg $^{-1}$) and Cd (0.01-7.01 mg kg $^{-1}$). Many of the topsoil samples from both regions exceeded Australian background levels and levels reported for the worlds soils.

This study highlights the potential danger of heavy metals accumulation, particularly Cd and Pb in vegetables grown in the vicinity of smelters. Vegetables from Boolaroo contained the highest levels of Cd (0.08-2.22 mg kg $^{-1}$ DW) and Pb (0.69-57.5 mg kg $^{-1}$ DW), and samples from Port Kembla had the highest level of Cu in all vegetable types. Almost all vegetables at Boolaroo exceeded Australian food standard guidelines for Cd and Pb. The site specific risk in growing vegetables in areas close to smelters and industry in general should be incorporated into the Australian Food standard guidelines to highlight and minimise the potential health risks of ingesting vegetables containing high levels of heavy metals.

Further research should consider variations in uptake between different species, the levels of metals present in the atmosphere (quantified) and the difference in vegetable uptake between soil and foliar mechanisms.

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