4-1-2011

Compost Application Affects Metal Uptake in Plants Grown in Urban Garden Soils and Potential Human Health Risk

Hollydawn Murray

Trevor A. Pinchin

Sheila M. Macfie
smacfie@uwo.ca

SOILS, SEC # • RESEARCH ARTICLE

Compost application affects metal uptake in plants grown in urban garden soils and potential human health risk

Hollydawn Murray • Trevor A. Pinchin • Sheila M. Macfie

H. Murray • T. A. Pinchin • S. M. Macfie (✉)

Department of Biology, University of Western Ontario, London, ON, N6A 5B7, Canada

e-mail: smacfie@uwo.ca

H. Murray

Present address: Hollydawn Murray, The National University of Ireland Galway, Earth and Ocean Science, University Road, Galway, Ireland

(✉) **Corresponding author:**

Sheila M. Macfie

Phone: 1-519-661-2111 ext. 86487

Fax: 1-519-661-3935.

e-mail: smacfie@uwo.ca

Abstract

Purpose This study explores the effect of varying organic matter content on the potential human health risk of consuming vegetables grown in urban garden soils.

Materials and methods Metal accumulation among edible tissues of green bean (*Phaseolus vulgaris* L.), lettuce (*Lactuca sativa* L.) and carrot (*Daucus carota* L.) was determined for plants grown in five urban garden soils amended with 0, 9, or 25% (v/v) compost. Potential risk to human health was assessed by calculating a bioconcentration factor and a hazard quotient.

Results and discussion Overall, the consumption of lettuce and green bean pods grown in some urban gardens posed a potential human health risk due to unacceptably high concentrations of cadmium or lead. In many cases, compost amendment increased the accumulation of metals in the vegetables. Even in soils considered uncontaminated by current guidelines, some hazard quotients exceeded the threshold value of 1. The compost used in this study had a high fulvic acid to humic acid ratio, which may explain increased concentrations of metals in plants grown in compost-amended soils.

Conclusions These results indicate a need to include soil characteristics, specifically organic matter quality, when setting threshold criteria for metal content of urban garden soils.

Keywords Fulvic acid • Humic acid • Metal contamination • Organic matter • Risk assessment • Urban gardens

1 Introduction

Urban soils are often enriched in metals (reviewed in Charlesworth et al. In press) and are a major site for human exposure to metals (De Miguel et al. 2007 and references therein). Soil metal contamination has the potential to be a serious public health issue, especially if edible plants are grown in these soils. Elevated concentrations of Cd in soils used to grow rice (*Oryza sativa* L.) led to human renal tubular dysfunction among Asian families (Kasuya 2000). Pruvot et al. (2006) calculated that the consumption of homegrown vegetables and crops (lettuce, leeks, cereals) in Northern France was a major contributor to total Cd and Pb exposure. Similar reports have been made for urban garden crops grown in France (Albering et al. 1999), United Kingdom (Hough et al. 2003), USA (Finster et al. 2004) and Australia (Kachenko and Singh 2004).

The decline in agricultural soil productivity due to erosion, runoff and loss of organic matter (OM) has stimulated interest in OM amendments including municipal organic waste, sewage sludge, agricultural waste, animal manure and industrial byproducts (Stevenson 1994). As in agriculture, compost application is the most common input of OM to urban gardens. Soil OM improves soil structure through the formation of cationic bridges (Hernando et al. 1989). It also increases soil fertility and water retention, and influences chemical speciation (Soumare et al. 2003).

Research on the role of OM in metal mobility presents apparently contradictory results. Soil OM has a high binding capacity for cationic and organic contaminants (Stevenson 1994), which might lead to immobilization of metal ions. For example, compost amendments significantly reduced metal accumulation by vegetables and human exposure to As (Cao and Ma 2004). In other studies, however, the degradation of OM released low molecular weight organic acids (such as malate and citrate) that bound metals and increased metal solubility. For example, a drastic increase in As leached from soils was observed following the addition of compost (Mench et al. 2003). Furthering the discrepancy, Fitz and Wenzel (2002) concluded that OM did not significantly affect As movement in soils. These differences reported for As have also been reported for other metals. For example, McBride et al. (1997) modeled the solubility of metals in soil solution in response to total metal content, pH and OM. While OM could be used to model Cu solubility for one data set, in which Cu was the only soil contaminant, they failed to find a consistent influence of OM on Cd, Cu, Pb and Zn solubility in the second data set, in which a range of soils contaminated by a number of metals was used. The lack of a clear relationship between OM and metal solubility is likely due to variations in the composition of the OM, specifically the proportions of dissolved and solid OM.

The majority of OM exists in the solid phase rather than in solution (DeBoodt et al. 1990), as a result it can form various complexes and may be insoluble, protonated, bound to the interlayer of clay minerals or adsorbed on clay or oxide surfaces (Sauvé et al. 1997). Many studies have implicated solid phase OM in the retention, decreased mobility and reduced bioavailability (i.e., reduced uptake into plants) of metals (Lion et al. 1982; Sanders 1980; Strawn and Sparks 2000).

Dissolved organic matter (DOM) is composed of several small molecules and is functionally defined as that which can pass through a 0.45 μm filter (Stevenson 1994). The proportion of DOM in soils is small when compared to the solid phase OM and/or the mineral matrix. Regardless, soil DOM influences important soil functions including physical stability (Rillig and Steingberg 2002). Up to 70% of DOM consists of humic (HA) and fulvic (FA) acids (Weng et al. 2002). These low molecular weight acids have carboxyl groups which attribute binding capacity, where the maximum binding capacity of the humic substance for any metal ion is approximately equal to the number of acidic functional groups (Stevenson 1994). Complexation of HA and FA with metal ions can alter the solubility of both the ligand and the bound species (Piccolo et al. 1992).

Among urban gardeners, compost is often proposed as a suitable material for vitalizing the soil. Traditionally, compost amendments are believed to immobilize metals thereby reducing toxicity. However, the type and quality of the compost will determine its effect on metal solubility. For example, Walker et al. (2004) found that both cow manure and composted leaves, when added to soil, resulted in decreased concentrations of Mn, Pb and Zn in shoots of *Chenopodium alba* L. but the concentrations were 2-10 times lower in plants grown with cow manure. In addition, amendment with cow manure resulted in 50% lower concentrations of Cu in the shoots whereas composted leaves resulted in a 25% increase. This contrasting effect of the two soil amendments was attributed to the cow manure being able to keep the soil pH above 6.0 while the compost-treated soil reached a pH of 4.4 after 83 days. In addition to the effects of compost on soil pH, the relative proportions of solid phase OM and DOM in the compost might affect metal accumulation in edible tissues and consumption of such vegetables could pose a risk to human health.

Risk assessment aims to characterize the potential adverse health effects of human exposures to environmental hazards (Markus and McBratney 2001). Quantitative guidelines for assessing risks associated with soil contamination are difficult to establish due to the complexity of the system. One solution is to establish maximum acceptable concentrations of metals in soils to be used for agriculture (cf., CCME 2006). Such guidelines are generally based on simplified assumptions about soil types and site conditions (Grasmuck and Scholz 2005) and thus may over- or underestimate potential risk. A second approach is to calculate a bioconcentration factor, which describes the concentration of a metal in the plant relative to the concentration in the soil (e.g., Antunes et al. 2006); the higher the bioconcentration factor, the more mobile the metal. A more direct, but labor-intensive, approach involves calculating a hazard quotient: the ratio of the amount of metal in a serving of food to the amount of metal known to be hazardous as determined through toxicity tests (Pierzynski et al. 2005).

In this study, the effect of compost amendments on bioconcentration factors and hazard quotients for selected vegetable species grown in metal-enriched soils was measured in order to assess the need to include OM when setting guidelines for urban garden soils.

2 Materials and methods

2.1 Soil preparation

Soils were obtained from the topsoil layer (25 cm) of three urban gardens in Montréal, QC: Baldwin (W), Despina (D), and St. Gerard (S). Two other soils were obtained from the Blackfriar's community garden in London, ON. One of these samples was taken from the garden plot (A), the other was taken from under the local compost pile (B). Compost, consisting of decomposed grass clippings and leaves that were collected from lawns and flower gardens on the university campus, was obtained from the University of Western Ontario Physical Plant compost pile, London, ON. The open compost pile was in a field at the edge of campus approximately 200 m from the nearest road and contained materials 3-4 years old. The top 20-40 cm of compost were removed prior to collecting compost for this experiment. All samples were air-dried and sieved to <2 mm as per MITHE guidelines (MITHE 2009). Sieved compost was thoroughly mixed with sieved soils to yield three proportions of compost (0, 9 and 25%). These mixtures represent the range of proportions of compost that an urban gardener might mix into the soil. The 15 soil/compost mixtures (5 soils x 3 compost mixtures) are henceforth referred to as the experimental soils.

2.2 Soil characterization

2.2.1 Metal content of the soil

Acid digestion for metal content followed the United States Environmental Protection Agency (US EPA) test method SW-846 (US EPA 2005). This procedure extracts all metals except those tightly bound to silicates, which are not bioaccessible under natural conditions. For three replicates of each of the 15 experimental soils and of the compost, 1.0 g soil and 1 ml OmniTrace® nitric acid (EMI Chemicals Inc., Gibbstown, USA) were placed in a glass test tube capped with a glass marble. Samples sat overnight at room temperature, then were digested at 100^{o}C until the vapors were clear (approx. 3 h). After cooling to room temperature, samples were filtered (qualitative paper #413, VWR International, Mississauga, Canada) then brought to a final volume of 50 ml with distilled water. Controls of distilled water, HNO_3, and Montana Soil (Standard Reference Material 2711, National Institute of Standards and Technology, Gaithersburg, USA) were similarly processed and analyzed. Digested samples were stored at 4^{o}C until analyzed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima-3300 DV ICP-OES, RF Generator Power-1300 Watts, Gas Flow Rate-15 l min^{-1}, Auxiliary Flow Rate- 0.5 l min^{-1}). One out of every 20 samples was run in duplicate; each set of duplicate values varied by $\leq$ 0.8% of each other. The following elements were quantified: Cd, Cu, Pb and Zn. The instrumental detection limits, as well as the analytical values for reagent blanks and NIST standard reference material are listed in Table 1.

2.2.2 Other physicochemical properties of the soil

Triplicate samples of the 15 experimental soils and of the compost were analyzed for four soil properties. Organic matter content was measured via loss on ignition at 500ºC for 12 h (Heiri et al. 2001). Soil conductivity was measured after equilibration for 30 min in deionized water at a 10:1 liquid: soil ratio with a HI 8033 electrode (Hanna Instruments, Laval, Canada) calibrated at 25ºC and 1413 $\mu S\ cm^{-1}$. The supernatants of these solutions were then measured for pH using a glass electrode calibrated at pH 4 and 10. Soil texture was determined using a sedimentation method adapted from Diaz-Zorita et al. (2002), which involved physical fractionation of sand, silt and clay particles suspended in 1% sodium pyrophosphate.

2.2.3 Soil organic matter extraction and fractionation

Concentrations of FA and HA in the experimental soils and compost were determined in triplicate following an adapted method of Bourbonniere and Creed (2006). After preliminary extraction tests, 6 g of each sample were shaken (145 rpm) at ambient temperature in 200 ml of deionized water for 12 h. The resulting extracts represent the DOM that might be present in the rhizosphere. Extracts were filtered successively through three media: (1) nominal 1.5 μm glass-fibre pad (Whatman 934-AH), (2) nominal 0.5 μm glass-fibre pad (Macherey-Nagel GF2), (3) sterile 0.45 μm polysulfone membrane. To minimize contamination with airborne microbes, the final filtration was conducted in a sterile laminar-flow hood. Subsamples of each whole filtered extract (WF) were acidified to pH <2 using 1 N HCl and stored at 4°C for 24 h. These samples were then filtered through sterile 0.45 μm polysulfone membrane to collect the fraction of DOM characterized by FA. Following filtration, both WF and FA samples were analyzed for DOC using a Shimadzu TOC-5000A C analyzer, after dilution with Milli-Q water and removal of dissolved inorganic C by acidification and sparging. The concentration of total DOC is the value obtained from the WF fraction, the concentration of FA is the value obtained from the FA fraction, and the concentration of HA is the difference between WF and FA.

2.2.4 Chemical speciation and distribution modeling

Chemical speciation and distribution modeling (NICA-Donnan) of Cd, Cu, Pb, and Zn was performed using Visual MINTEQ ver 3.0 (http://www.lwr.kth.se/English/OurSoftware/vminteq/). Measured concentrations of trace metals, HA, FA and pH were fixed based on preliminary soil measurements. The model was used to estimate the impacts of HA and FA on metal solubility.

2.3 Pot trials

Three crop species, green bean (*Phaseolus vulgaris* L.), lettuce (*Lactuca sativa* L.) and carrot (*Daucus carota* L.) were chosen for study because they are commonly grown in urban gardens in Canada and they represent a seed, leaf and root crop, respectively.

Seeds were imbibed on moist filter paper then potted in each of the 15 experimental soils, one plant per 10 cm diameter pot, 3 replicates per soil type. The pots were placed in a growth chamber with cool white fluorescent lighting, on a 16 h photoperiod with day and night temperatures set to 20 and 16ºC, respectively. Pots were watered daily to 75% field capacity with deionized water. Plants were harvested upon maturation of the edible tissues: green bean pods, lettuce leaves and carrot tap roots were harvested at 64, 55 and 79 days of growth, respectively. Lettuce leaves and carrot roots were rinsed in deionized water to remove soil and blotted dry. All plant tissues were dried to a constant weight in a 60°C oven.

2.4 Plant tissue analysis

Plant tissues were analyzed for total metal content following EPA test method SW-846 (US EPA 2005) in the same manner as for soil samples, with 0.1 g dry tissue being digested in 1 ml OmniTrace® nitric acid. Controls of distilled water, HNO_3, and tomato leaves (Standard Reference Material 1573a, National Institute of Standards and Technology, Gaithersburg, USA) were similarly processed and analyzed (Table 1). The metal content of digested plant tissues was determined using ICP-OES, as described above for soil.

2.5 Statistical analysis

Soil metal content and general soil properties were analyzed by one-way ANOVA. For all ANOVA where significant ($P < 0.05$) main effects were detected, Tukey's test of multiple comparisons was used. Pearson product-moment correlation coefficients were used to measure the strength of relationship between BCF and concentrations of soil HA and FA. Correlations were declared significant at $P < 0.05$.

All statistics were performed using SigmaPlot Version 11. Normality, homogeneity of variance, and correlation tests were undertaken prior to data testing. For some data sets, a natural logarithm transformation of the data was used to satisfy the assumptions of normality and variance homogeneity.

2.6 Bioconcentration factors

To assess the relative mobility of Cd, Cu, Pb and Zn across soil types, bioconcentration factors (BCF) were calculated using equation 1 (modified from Antunes et al. 2006):

$$\text{[1]} \qquad BCF = M_e / M_s$$

Where M_e = mean concentration of the metal in the edible tissue (mg kg^{-1} dry weight) and M_s = mean concentration of the metal in the soil (mg kg^{-1} dry soil). BCF values above 1.0 indicate the concentration of metal in the tissue is higher than that of the soil.

2.7 Screening level risk evaluation to human health

In terms of potential risk to human health, ingestion of vegetables was the only exposure pathway considered in this study. Although not all of the food ingested is bioavailable (i.e. absorbed by the body from the intestinal tract) to humans, the rate of consumption of contaminated foods is a valuable estimate of potential health risk (Pierzynski et al.2005). The average daily dose (ADD) was calculated using equation 2 (modified from Sipter et al. 2008):

[2] $$ADD = (C_{veg} \times Y_{veg}) / BW$$

Where C_{veg} = concentration of the metal in the edible tissue (mg kg^{-1} fresh weight), Y_{veg} = average amount of the vegetable consumed (kg day^{-1}), and BW = average bodyweight (kg). The ADD was calculated for Cd, Cu, Pb and Zn. The ADD for males is slightly higher than that of females due to differences in serving size (8 servings of vegetables per day for females and 10 servings for males) and average body mass (69.4 kg for females, 82.6 kg for males). Because ADD for males are higher, they will be used here as a conservative estimate of potential risk. Daily consumption values were based on Canada's Food Guide (Health Canada 2008), with the assumption that an individual would eat the recommended amount of vegetables per day by consuming only beans, only lettuce or only carrots.

The non-carcinogenic risk of vegetable consumption was characterized using a hazard quotient (HQ), which is the ratio of the ADD to the reference dose (RfD) for each metal (Pierzynski et al. 2005). A reference dose corresponds to the maximum amount of a metal that can safely be consumed per day, per kg body weight. Reference doses were obtained from the International Toxicity Estimates for Risk (ITER) database (TERA 2010): 0.001 mg kg^{-1} day^{-1} for Cd; 0.14 mg kg^{-1} day^{-1} for Cu; 0.036 mg kg^{-1} day^{-1} for Pb;

and 0.3 mg kg^{-1} day^{-1} for Zn. If the HQ is greater than 1, then the ADD of that particular metal exceeds the RfD, indicating that there is a potential risk associated with consumption of that food.

3 Results

3.1 Soil characterization

Soils W, D, S and B had concentrations of at least one metal above the Canadian Soil Quality Guidelines (Fig 1). In soil W, concentrations of Cd and Zn were just over the CCME (2006) limits and the concentration of Pb was approximately 2 times the limit. Soil D had 2.5 times the limit for Pb and was just over the limit for Zn. Soil S was the most contaminated of the garden soils, with 6 times more Cu, 5 times more Pb and 1.3 times more Zn than the recommended maximum for agricultural soil. The concentrations of metals in soil A were well below the CCME (2006) limits. Soil B had 1.6 times the acceptable concentration of Pb. In general, the concentrations of metals in the soil were diluted as compost was added (Fig 1). A notable exception was for Cd in soils D, S, A and B, for which background concentrations of Cd were 2–5 times lower than in the compost.

Fifteen experimental soils and the compost were analyzed for organic matter content, conductivity, pH and texture (Table 2). OM content ranged from 6.9% to 18.5% in the experimental soils. The compost OM was 30.8%. Conductivity values were between 400 μS cm^{-1} and 1330 μS cm^{-1}. Only soil B and the compost had conductivity and OM content values significantly higher ($p<0.001$) than the others. All experimental soils had a pH around 8; compost had a significantly lower pH (7.3, $p<0.001$). Decreases in pH and percent sand were recorded for all compost additions, yet no reductions were significant. These changes in soil properties as a result of compost additions were due to a dilution effect caused by mixing of the compost with the soils. Based on proportions of sand, silt and clay, soils W, D and S were identified as sandy loam, soil A was loamy sand, and soil B was sand. The concentrations of each of the DOC fractions in solution for the 15 experimental soils and the compost are shown in Fig. 2. The concentration of FA in the compost was at least twice the amounts in soils W, D, S, and A; therefore, FA increased by 25–50% with compost amendment in these soils. The concentration of HA in the compost was slightly lower than the concentrations in soils W, D, S and A; subsequently, addition of compost had no significant effect on HA in those experimental soils.

Chemical speciation and distribution modeling was used to predict free metal ions as well as dissolved organic ligands in the experimental soils (Table 3). In soils W, D, A and B over 93% of the total Cd was predicted to be the free ion. In soil S, the predicted proportion of free Cd^{2+} was 21%, 51% and 86% in soils amended with 0, 9 and 25% compost, respectively. The only metal that had a consistently high proportion bound to FA and HA was Cu; the estimated distributions of Cu were more evenly spread among Cu^{2+}, FA-Cu and HA-Cu, and did not vary with compost amendment except for soil S in which free Cu^{2+} increased from 11.5 to 71.6% of the total Cu. For Pb and Zn, the patterns were similar to that of Cd, with most of the Pb (>81%) and Zn (>98%) being predicted to be in ionic form, except for soil S in which free ions were predominant only in the soil with the highest compost amendment.

3.2 Metal uptake by vegetables

Due to the large size of this data set (15 experimental soils x 3 vegetables x 4 metals = 180 average values), the individual concentrations of each metal in the plant tissues have not been included in this paper. In terms of risk assessment, the relative translocation of metals from soil to plants (BCF) and the amount of metal potentially consumed (HQ) are more relevant than the absolute concentration of metal; therefore, we will report only the ranges in metal concentration for each species.

3.2.1 Green bean

Concentrations of Cd in all green bean pods were under the limit of detection (i.e., <0.13 mg kg^{-1}). Concentrations of Cu in the bean pods ranged from 1.6 ± 0.1 to 3.2 ± 0.5 mg kg^{-1} and did not vary among experimental soils. Concentrations of Pb ranged from 0.6 ± 0.05 to 12.7 ± 12.3 mg kg^{-1}, with the lowest values being for bean pods grown in soil B. Concentrations of Zn ranged from 7.8 ± 5.2 to 22.8 ± 1.0 mg kg^{-1}, with the highest values being for bean pods grown in soils W and B, and the lowest values being from soil A. Addition of compost did not affect the concentrations of Cu, Pb or Zn in the bean pods.

The BCF values for green bean pods are shown in Fig. 3a, d, g and j. It was not possible to calculate BCF for Cd because that metal was not detected in this tissue. The BCF values for Cu, Pb and Zn were all below 0.4, indicating that these metals did not bioconcentrate in the bean pods. Addition of compost resulted in increased translocation of Cu into the bean pods in all soils except W (see Fig. 3d), increased Pb in bean pods grown in soils W and B (see Fig. 3g), and increased Zn in bean pods from soils W, S and B (see Fig. 3j). The only case for which addition of compost reduced the metal concentration in the bean pods was for Zn in soil A (see Fig. 3j).

Over all soils, no significant relationship was found between the green bean BCF and FA in the soil for Cd (below detection limit), Cu, Pb or Zn (Table 4). The only metal with a significant relationship to HA was Cu. Given the estimated proportions of metals bound to FA and HA responded very differently to compost addition in soil S (see Table 3), additional correlations were calculated for this soil independently of the others. Within soil S, the concentration of FA was positively correlated with the BCFs for Cu and Zn (see Table 4).

3.2.2 Lettuce

Lettuce sown in soil S with 25% compost did not germinate. The treatment was repeated twice and, while some cotyledons emerged, no seedlings survived this soil/compost combination. Concentrations of Cd in lettuce ranged from 0.4 ± 0.2 to 1.6 ± 0.5 mg kg^{-1}, with the lowest values being for lettuce from soil B. Concentrations of Cu in lettuce ranged from 2.8 ± 0.3 to 6.4 ± 0.9 mg kg^{-1} and the highest value was for lettuce grown in soil S with 9% compost. Concentrations of Pb ranged from 7.1 ± 0.1 to 13.4 ± 1.3 mg kg^{-1}, with concentrations not varying among soils. Concentrations of Zn ranged from 13.3 ± 5.8 to 32.3 ± 4.3 mg kg^{-1}, and did not vary among soils. Addition of compost to soil W resulted in a 37% decrease in Cd concentration and 22 and 34% percent increases in concentrations of Cu and Pb, respectively. In soil S, 9% compost had no effect on Cd but caused 27, 48 and 37% increases in concentrations of Cu, Pb and Zn, respectively.

Lettuce BCF values are plotted in Fig. 3b, e, h and k. BCF values for Cd (see Fig. 3b) were generally higher than those of the other metals, indicating that Cd is the most mobile element of the four. Nonetheless, all BCF values were below 1.0, indicating that the metals did not bioaccumulate in lettuce. Addition of compost resulted in higher Cd BCF values in soils D, A and B (see Fig. 3b). Compost had little effect on the Cu BCF, except in soil A for which the lettuce grown in the 25% compost mixture had a 7-fold lower BCF value and soil B for which addition of compost resulted in 30% higher BCF values (see Fig. 3e). Addition of compost had no effect on the BCFs for Pb and Zn with one exception; lettuce grown in soil W with 9% compost had an unexplained 40% increase in the BCF for Pb.

In lettuce, FA in the soils was positively correlated with Zn, and HA was negatively correlated with Cd (see Table 4). No other significant relationships were found between HA or FA in soil and lettuce BCF. When soil S was analyzed independently, positive correlations were found between FA and the BCFs for Pb and Zn.

3.2.3 Carrot

Concentrations of Cd and Pb in all carrots were below the detection limits (i.e., <0.1 and < 0.4 mg kg^{-1}, respectively). Concentrations of Cu ranged from 1.9$\pm$0.4 to 9.0$\pm$0 mg kg^{-1}, with the highest values associated with soils S and B. Concentrations of Zn ranged from 13.7$\pm$0.2 to 29.7$\pm$7.4 mg kg^{-1}, with the highest values being for carrots grown in soil S. Addition of compost resulted in a 46% decrease in the concentrations of

Cu for carrots grown in soils W and A, and a 60% decrease in the concentration of Cu for soil B. Compost addition had no effect on concentrations of Zn in carrot.

Neither Cd nor Pb were measured in carrots, hence the corresponding BCF values could not be calculated. Neither Cu (Fig. 3f) nor Zn (Fig. 3l) bioaccumulated in carrot. Addition of compost reduced the BCF for Cu for carrots grown in soil D, but increased the BCFs for Cu in soils S and B (Fig. 3f). Compost resulted in lower BCF values for Zn in soils W and D and a higher BCF value in soils A and B (Fig. 3l).

No significant relationship was found between BCF and either HA or FA in the soils for carrot (see Table 4). However, in soil S a positive correlation was found for FA and the BCF for Cu.

3.3 Screening level risk evaluation to human health

3.3.1 Green bean

Estimated HQ values for bean are shown in Fig. 4a, d, g and j. The only metal with some HQs exceeding the threshold value of 1 was Pb (see Fig. 4g). The largest potential risk was associated with the ingestion of beans grown in soils W and A containing 25% compost, and soils D and S with 0 or 9% compost. Although soils A and B are considered uncontaminated by Pb under the current guidelines (CCME 2006), the HQs for Pb approached or exceeded the threshold value of 1 when 25% compost was added. No bean presented a potential risk with respect to consuming an unacceptable amount of Cd, Cu or Zn. Even in soils considered contaminated by Cd (W), Cu (S) or Zn (W, D, and S) beans did not have corresponding HQs greater than 1, suggesting beans grown in these soils are not likely to pose a human health risk for these metals.

3.3.2 Lettuce

The HQ values for lettuce are plotted in Fig. 4b, e, h and k. The HQs for Cd (see Fig. 4a) and Pb (see Fig. 4h) exceeded the threshold value of 1 in all experimental soils. The HQs for Cd ranged from 3.5–10.4. Even in soils considered uncontaminated by Cd (D, S, A, and B), Cd posed a potential human health risk. While statistical analysis of HQ values was not possible because HQs were calculated using average metal concentrations, compost appeared to decrease the HQ for Cd in soil W and increase the potential risk in soils D, S and A. Although the range in Pb HQs was less than those of Cd, there was a potential hazard associated with consuming lettuce grown in each of the soils; including soils A and B, which were below the CCME (2006) guideline for Pb. The only HQ that seemed affected by compost was in soil S with 9% compost, in which the HQ doubled relative to unamended soil. Lettuce did not pose a potential risk with respect to consuming an unacceptable amount of either Cu (Fig. 4e) or Zn (Fig. 4k); however, the corresponding HQs appeared to increase with compost amendment for plants grown in soil W, and with 9% compost in soil S.

3.3.3 Carrot

None of the HQs for carrot exceeded 0.15 (see Fig. 4c, f, i and l), indicating no potential human health risk associated with the consumption of carrots, even those grown in contaminated soils.

4 Discussion

4.1 Bioavailability of metals to plants as a function of soil physicochemistry

This study demonstrates that vegetables grown in contaminated soils accumulated metals, but the edible tissues with the highest concentrations of metals did not necessarily come from plants grown in the most contaminated soil. If there had been a positive relationship between concentrations of metal in the soil and metal bioavailability, then vegetables grown in soils with metals above agricultural limits set forth by the CCME (2006) might be expected to be unsafe for human consumption. Specifically, plants grown in soil S might be expected to pose the greatest potential risk to consumers, and plants grown in soil A might be expected to contain low concentrations of metals.

However, it would be naïve to think metal bioavailabilty should be directly proportional to the concentration of metal in the soils. Metal bioavailability is not only a function of total soil metal content but is also strongly influenced by soil properties such as pH and clay content. In general, metal solubility increases as pH decreases. The soils in this study had similar pH values (8.0 to 8.2); therefore, differences in metal uptake among the soils were not likely due to an influence of pH on metal solubility. Metal ions readily adsorb to clay micelles and they might be expected to be less available to plants grown in soil D, which had high clay content (27%) relative to the other soils (0–19%). Metal bioavailability also varies with OM content. Given the slightly lower pH (7.7 to 7.9) and the increased conductivity upon addition of compost, one might expect metals in amended soils to be more bioavailable (Sinha et al. 2006; Walter et al. 2006); however, these soils also have increased OM content, which could result in reduced metal bioavailability (Ali et al. 2004). BCFs were calculated in order to determine the relationship between metals in the soil and metal accumulation in the edible plant tissues.

For the most part, BCFs decreased with increasing soil metal for Cd, Cu, Pb, and Zn. For example, soil S had the highest concentrations of Cu, Pb and Zn but plants grown in soil S consistently had the lowest BCF values for these three metals. This is in agreement with Alam et al. (2003) who found that BCF values for As decreased as metal soil content increased. Sharma and Dubey (2006) reported similar results indicating that concentrations of Cd decreased in all plant parts as application rates of a multi-metal mixture increased. This concentration-dependant response of metals in multi-metal systems, such as the soils used here, is ascribed to competition of metal ions for exchange sites at the soil surface, as well as competition for transport at the root plasma membrane (Hart et al. 2002).

Across all soils and vegetables, the metals in increasing order of bioavailability were Cd > Zn > Cu > Pb. This is in accord with the order reported for five vegetables (including lettuce), grown in four soils determined by Murray et al. (2009) but in slight contrast to the order Cd > Cu > Zn > Pb observed by Intawongse and Dean (2006) for carrot, radish, lettuce and spinach. Compost amendment resulted in increased or equal BCF in all three vegetables with only five exceptions (indicated by grey boxes in Fig. 3), Ozores-Hampton et al. (1997) has also reported increased metal bioavailability to vegetables after compost amendment in spite of low compost metal concentrations. This suggests that increased bioavailability due to altered pH and/or conductivity might prevail over decreased metal availability arising from complexation with OM. However, the direct influence of compost composition (e.g., HA to FA content) on metal bioavailability is also important (Unsal and Ok 2001).

4.2 Influence of organic matter on bioavailability of metals to plants

Of the 45 vegetable/soil combinations reported in Fig. 3, edible tissue BCFs increased with compost amendment in 15 cases (indicated by the white boxes). Several studies have reported similar results for different vegetables including: Maftoun et al. (2004) who found increased uptake of Pb, Mn, Na, and Cl in spinach (*Spinacia oleracea*) where soil was amended with 80 Mg ha^{-1} of either composted municipal waste or poultry manure; Murillo et al. (1997) who determined 100 Mg ha^{-1} municipal solid waste increased both Zn and Cu accumulation in clover (*Trifolium repens*); and Warman and Rodd (1998) who observed increased plant Cu concentrations in corn (*Zea mays*), squash (*Cubcurbita maxima*) and potatoes (*Solanum tuberosum)* grown in agricultural soils amended repeatedly with levels of compost as low as 5 Mg ha^{-1}. However, these results are in direct contrast to those reported by Brown et al. (2005) who found that compost addition to contaminated urban soils greatly reduced Pb bioavailability, converting it from exchangeable to organic-bound forms. These apparently contradictory results can be partially explained when the dynamics of metal-DOM complexes in soil solution are considered.

It has been suggested that FA, unlike HA, is capable of increasing metal bioavailability (Plaza et al. 2006). Of the two, HAs have a higher molecular weight, proportionately fewer carboxyl groups and more S atoms (Plaza 2006; Stevenson 1994), which may result in a higher binding affinity for metal ions. The relative bioavailability of metals complexed with HA and FA has not been studied; however, toxicity of Cd and Zn to the green alga *Pseudokirchniella subcapita* was greatly reduced when the metal was complexed with HA as compared to FA (Koukal et al. 2003). In this study, measurements of HA and FA in the DOM compost fraction were used to assess compost quality. The average HA:FA ratio of 0.54 is far lower than the suggested mature ratio of 3.55 (He et al. 1995), indicating that the compost used was not fully decomposed. Thus the addition of compost, and subsequent increase in FA, in each of the amended soils may be responsible for the increased plant metal uptake upon compost addition observed in this study. However, when data from all soils were combined poor correlations between partitioning of the operationally defined DOM (HA and FA) and BCF\ of each metal were found (see Table 4). The only individual soil type with strong correlations between FA or HA and BCF was soil S, which had the lowest initial concentration of FA and the highest initial concentrations of metals. This indicates that FA is capable of keeping Cu, Pb and Zn in solution after dissolution from the solid phase.

Garcia-Mina (2006) determined that FA-Cu complexes are more stable than HA-Cu complexes in near-neutral soil solutions. Speciation modeling supported the relative higher affinity of HA compared to FA for metal ions, as well as the predominance of Cu complexation with FA and HA. With the exception of soil S, low proportions of Cd, Pb and Zn ions were predicted to be complexed with FA and HA. In soil S, not only were the proportions of free metal ions lower than in the other soils, addition of compost resulted in dramatic increases in estimated metal solubility. This increase may have been responsible for the toxicity to lettuce of soil S with 25% compost addition.

Despite the modeling results, FA was not consistently positively correlated with BCF values. This may be due to differences between the species' capacities to take up and translocate FA-metal complexes. For instance, if metal transport sites on carrot roots have an extremely low affinity for FA-Cu complexes, then increased FA could actually decrease Cu availability. Varied metal accumulation among the species within a single soil type supports this idea. In lettuce, the lack of correlation may simply be the result of a dilution effect. The amount of Cu added to the plant metal pool by FA may be small relative to the large biomass of lettuce but substantial in the lower biomasses of green bean pods and carrot.

While compost increased metal bioavailability in many cases, the pattern was not consistent within any one soil, metal or vegetable. Differences between plant species' ability to accumulate metals are widely recognized and so it should be no surprise that different responses to varying compost (especially FA content) additions also exist. This may be due to species differences in plant-induced changes in the rhizosphere. For example, it is possible that some species' roots produce exudates that alter rhizosphere chemistry such that FA- or HA-metal complexes are more (or less) stable. Metal concentration in the soil can also alter metal bioavailability. Stevenson (1994) theorized that DOM complexation of metals increases their solubility, mobility and availability under deficiency conditions while complexation of highly available metals results in a sequestering effect where soil metal is high. Further investigation is warranted to determine the merit of including OM and DOM status of the soil when setting guidelines for acceptable metal content.

4.3 Assessing risk to human health

Urban gardening has increased in popularity among many socioeconomic groups (Harris 2000). It is an important source of fresh produce and reduces food costs (Finster et al. 2004). In soils, OM enhances soil structure, retention of nutrients, microbial biodiversity and resistance to erosion (Jenny, 1961) and compost amendment has been shown to increase the bioavailability of N, P, K to plants (Chaoui et al. 2003).

However, one must balance the positive aspects of urban gardening with the potential hazards. Of particular interest, soils considered uncontaminated by Cd posed a potential health risk for consumers of lettuce. Soils D, S, A and B had less than 40% the allowable Cd, yet their lettuce HQs ranged from 3.5–10.5. In contrast, in soil D, which was considered mildly contaminated by Zn, all vegetables had HQs less than 1. Similarly, 5 vegetable species grown in an agricultural soil where Zn was 10% above the allowable limit had HQs below 1 (Murray et al. 2009). This is also in agreement with Sipter et al. (2008) who reported non-toxic concentrations of metals in vegetables that were grown in contaminated soils. Clearly, food safety guidelines that rely solely on metal content of the soil do not accurately reflect the potential risk to consumers.

The potential human health risk assessment in this study varied with vegetable species. Lettuce showed the highest HQs for all four metals and 50% of the samples analyzed were considered potentially hazardous. This is in contrast to green bean pods and carrot, where only 13% and 0% of samples analyzed, respectively, had HQs greater than 1. Harrison (2001) found similar results and concluded that plant leaves often have higher metal concentrations than stems, making leafy vegetables grown under contaminated conditions a greater potential risk to human health. Guidelines may have to differ among vegetable species or type of vegetable. As seen for green bean pods and lettuce, some crops accumulate potentially hazardous concentrations of metals in soils that are below current guidelines and some crops accumulate safe concentrations of metals in soils that appear toxic.

Ultimately, the goal of setting appropriate soil metal guidelines is fueled by the need to protect human health. Assuming a body weight of 86.2 kg, it is recommended that males consume 10 servings of vegetables per day from the nutritional point of view (Health Canada 2008). The human health risk assessment presented here assumes conservatively that this vegetable consumption is entirely green bean, carrot or lettuce. However, if the vegetables grown in this study contributed only 10% of the 10 serving daily diet, all corresponding HQs would fall below 1. It would be prudent to take daily vegetable servings from a variety of sources.

4.4 Future directions

The results of this study could not conclusively account for the change in bioavailability of metals to plants upon compost amendment. Although the compost used in this experiment contained no visible traces of plant material, its low HA:FA ratio (0.54) indicates that decomposition was not complete. Fresh organic wastes are rich in nonspecific soluble organic compounds such as amino acids and polysaccharides. These compounds can increase metal solubility immediately following addition to the soil via formation of soluble organo-metallic complexes (Shuman 1999). Similarly, the presence of numerous organic ligands (e.g., citric acid, oxalic acid, formic acid and succinic acid) in the rhizosphere are known to increase leaching of Zn, and presumably other metals, from soil (Burckhard et al. 1995). Thus there is need for further study to examine the character and concentration of these organic ligands in compost amendments and their correlation, if any, with soil metal bioavailability.

Concentrations of HA did not vary sufficiently among the experimental soils in this study to determine its impact on metal bioavailability to plants. In contaminated soils, Chen (1996) and Halim et al. (2003) found that HA addition decreased metal toxicity while Christensen and Christensen (1999) concluded that HA can also increase metal bioavailability as fragments of HA form metal chelates which are readily taken up by plants. Humic acid may be important in the solubility of certain metals only, and further investigation is warranted.

5 Conclusions

This urban garden study demonstrated that three vegetables grown in contaminated soils accumulated metals to varying levels. In general, our data suggest that leafy crops are most likely to pose a potential health hazard to consumers.

The application of a FA-rich compost often increased the BCFs of Cd, Cu, Pb and Zn for green bean pods, lettuce leaves and carrot roots. This highlights the importance of DOM surface sites in trace element bioavailability and the potential for FA to alter metal solubility in the rhizosphere. While metal transfer from amended soil to edible tissues was not consistently dominated by either DOM fraction, our results suggest the best method to reduce bioconcentration of metals is to secure composts that are sufficiently mature (e.g., relatively high HA:FA ratio) and low in metal content.

While urban gardens are not generally regarded as toxic zones, four of the five urban gardens studied were contaminated with at least 1 metal above the CCME (2006) agricultural limit. Screening level risk evaluation revealed that consumption of green bean and lettuce leaves, but not carrot roots, grown in some soils posed a potential human health risk for at least 1 metal, though some soils were considered safe by CCME standards. The majority of potential health risks occurred in soils amended with 25% compost. These results emphasize the need for more specific guidelines. While a new urban garden risk assessment model must be generic enough to satisfy a wide range of applications and not involve complex measurements, the results of this study support the merit of including soil type and/or crop species while formulating guidelines. The ultimate goal is to increase confidence in assessing potential risks to human health.

Acknowledgements This project was supported by the Natural Science and Engineering Research Council (NSERC) Discovery Grant Program, the Canadian NSERC Metals in the Human Environment (MITHE) Strategic Network (a full list of sponsors is available at www.mithe-sn.org) and the Western Graduate Thesis Research Award. Many thanks go to Mr. Jim Galbraith from the University of Western Ontario (UWO) Physical Plant for supplying compost, the Biotron Research Facility at UWO for ICP-OES analyses, and the Catchment Research Facility at UWO for DOC analyses.

References

Alam MGM, Snow ET, Tanaka A (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. Sci Total Environ:308:83–96

Albering HJ, van Leusen SM, Moonen EJ, Hoogewerff JA, Kleinjans JCS (1999) Human health risk assessment: a case study involving heavy metal soil contamination after the flooding of the river Meuse during the winter of 1993–1994. Environ Health Perspect 107:37–43

Ali NA, Ater M, Sunahara GI, Robidoux PY (2004) Phytotoxicity and bioaccumulation of copper and chromium using barley (*Hordeum vulgare* L.) in spiked artificial and natural forest soils. Ecotoxicol Environ Saf 57:363

Antunes PMC, Berkelaar EJ, Boyle D, Hale B, Hendershot W (2006) The biotic ligand model for plants and metals: technical challenges for field application. Environ Toxicol Chem 25:875–882

Bourbonniere RA, Creed IF (2006) Biodegradability of dissolved organic matter extracted from a chronosequence of forest-floor materials. J Plant Nutr Soil Sci 169:101–107

Brown S, Christensen B, Lombi E, McLaughlin M, McGrath S, Colpaert J, Vangronsveld J (2005) An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn *in situ*. Environ Pollut 138:34–45

Burckhard SR, Schwab AP, Banks MK (1995) The effects of organic acids on the leaching of heavy-metals from mine tailings. J Hazard Mater 41:135–145

Cao X, Ma LQ (2004) Effects of compost and phosphate on plant arsenic accumulation from soils near pressure-treated wood. Environ Pollut 132:435–442

CCME (Canadian Council of Ministers of the Environment) (2006) Canadian environmental quality guidelines, Ottawa, Canada. http://ceqg-rcqe.ccme.ca/. Accessed 14 August 2010

Chaoui HI, Zibilske LM, Ohno T (2003) Effects of earthworm casts and compost on soil microbial activity and plant nutrient availability. Soil Biol Biochem 35:295-302.

Charlesworth S, De Miguel E, Ordonez A (In press) A review of the distribution of particulate trace elements in urban terrestrial environments and its application to considerations of risk. Environ Geochem Health DOI 10.1007/s10653-010-9325-7

Chen Y (1996) Organic matter reactions involving micronutrients in soils and their effect on plants. In: Piccolo A (ed) Humic substances in terrestrial ecosystems. Elsevier, Amsterdam, pp 507–530

Christensen JB, Christensen TH (1999) Complexation of Cd, Ni,and Zn by DOC in polluted groundwater: a comparison of approaches using resin exchange, aquifer material sorption, and computer speciation models (WHAM and MINTEQA2). Environ Sci Technol 33:3857–3863

DeBoodt MF, Hayes M, Herbillon A (1990) Soil colloids and their associations in aggregates. Plenum Press, New York

De Miguel E, Iribarren I, Chacon E, Ordonez A, Charlesworth S (2007) Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66:505-533

Diaz-Zorita M, Perfect E, Grove JH (2002) Disruptive methods for assessing soil structure. Soil Tillage Res 64:3–22

Finster ME, Gray KA, Binns HJ (2004) Lead levels of edibles grown in contaminated residential soils: a field survey. Sci Total Environ 320:245–257

Fitz WJ, Wenzel WW (2002) Arsenic transformations in the soil-rhizosphere-plant system: fundamentals and potential application to phytoremediation. J Biotechnol 99:259–278

Garcia-Mina JM (2006) Stability, solubility and maximum metal binding capacity in metal-humic complexes involving humic substances extracted from peat and organic compost. Org Geochem 37:1960–1972

Grasmuck D, Scholz RW (2005) Risk perception of heavy metal soil contamination by high-exposed and low-exposed inhabitants: the role of knowledge and emotional concerns. Risk Anal 25:611–622

Halim M, Conte P, Piccolo A (2003) Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. Chemosphere 52:265–275

Harris M (2000) Urban Edens: community gardens help neighborhoods nourish the body, heal the spirit and enrich the world. Veg Times 271:79–84

Harrison PTC (2001) Health effects of environmental chemicals. In: Harrison RM (ed) Pollution: causes, effects and control. Royal Society of Chemistry, Cambridge, pp 500–523

Hart JJ, Welch RM, Norvell WA, Kochian LV (2002) Transport interactions between cadmium and zinc in roots of bread and durum wheat seedlings. Physiol Plant 116:73–78

He X, LoganTJ, Traina SJ (1995) Physical and chemical characteristics of selected US municipal solid waste composts. J Environ Qual 24:543–552

Health Canada (2008) Canada Food Guide http:// www.healthcanada.gc.ca/foodguide/ Accessed 12 August 2010

Heiri O, Lotter AF, Lemcke G (2001) Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J Paleolimnol 25:101–110

Hernando S, Lobo MC, Polo A (1989) Effect of the application of a municipal refuse compost on the physical and chemical properties of a soil. Sci Total Environ 81:589–

96.

Hough RL, Young SD, Crout NMJ (2003) Modeling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm. Soil Use Manage 19:19–27

Intawongse M, Dean JR (2006) Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. Food Addit Contam 23:36–48

Jenny H (1961) Derivation of state factor equations of soils and ecosystems. Soil Sci Soc Am Proc 25:385–358

Kachenko A, Singh B (2004) Heavy metals contamination of home grown vegetables near metal smelters in NSW. Super Soil. 3rd ed. Australian New Zealand Soils Conference, University of Sydney, Australia http://www.regional.org.au/au/asssi/. Accessed 14 August 2010

Kasuya M (2000) Recent epidemiological studies on itai-itai disease as a chronic cadmium poisoning in Japan. Water Sci Technol 42:147–154

Koukal B, Guéguen C, Pardos M, Dominik J (2003) Influence of humic substances on the toxic effects of cadmium and zinc to the green alga *Pseudokirchneriella sucapitata*. Chemosphere 53:953–961

Lion LW, Altmann RS, Leckie JO (1982) Trace-metal adsorption characteristics of estuarine particulate matter - evaluation of contributions of Fe/Mn oxide and organic-surface coatings. Environ Sci Technol16:660–666

Maftoun M, Moshiri F, Karimian N, Ronaghi AM (2004) Effects of two organic wastes in combination with phosphorus on growth and chemical composition of spinach and soil properties. J Plant Nutr 27:1635–1651

Markus J, McBratney AB (2001) A review of the contamination of soil with lead II, spatial distribution and risk assessment of soil lead. Environ Int 27:399–411

McBride M, Sauvé S, Hendershot W (1997) Solubility control of Cu, Zn, Cd and Pb in contaminated soils. Eur J Soil Sci 48:337–346

Mench M, Bussiere S, Boisson J, Castaing E, Vangronsveld J, Ruttens A, De Koe T, Bleeker P, Assuncao A, ManceauA (2003) Progress in remediation and revegetation of the barren Jales gold mine spoil after in situ treatments. Plant Soil 249:187–202

MITHE (Metals in the Human Environment Strategic Network) (2009) Quality Assurance/Quality Control. http://mithesn.org/data_management/qa_qc.cfm/. Accessed 14 August 2010

Murillo JM, Cabrera F, Lopez R (1997). Response of clover *Trifolium fragiferum* L cv 'Salina' to a heavy urban compost application. Compost Sci Util 5:15–25

Murray H, Thompson K, Macfie SM (2009) Site- and species-specific patterns of metal bioavailability in edible plants. Botany 87:702–711

Ozores-Hampton M, Hanlon E, Bryan H, Schaffer B (1997) Cadmium, copper, lead, nickel and zinc concentrations in tomato and squash grown in MSW compost-amended calcareous soil. Compost Sci Util 5:40–46

Piccolo A, Zaccheo P, Genevini PG (1992) Chemical characterization of humic substances extracted from organic-waste-amended soils. Bioresour Technol 40:275–282

Pierzynski GM, Sims JT, Vance GF (2005) Soils and environmental quality. Taylor and Francis, Boca Raton

Plaza C, Hernandez D, Fernandez JM, Polo A (2006) Long-term effects of amendment with liquid swine manure on proton binding behavior of soil humic substances. Chemosphere 65:1321–1329

Pruvot C, Douay F, Hervé F, Waterlot C (2006) Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas. J Soils Sediments 6:215–220

Rillig MC, Steinberg PD (2002) Glomalin production by an arbuscular mycorrhizal fungus: a mechanism of habitat modification? Soil Biol Biochem 34:1371–1374

Sauvé S, McBride MB, Hendershot WH (1997) Speciation of lead in contaminated soils, Environ Pollut 98:149–155

Sanders JR (1980) The use of adsorption equations to describe copper complexing by humified organic matter. J Soil Sci 31:633–641

Sharma P, Dubey RS (2006) Cadmium uptake and its toxicity in higher plants. In: Khan NA, Samiullah (eds) Cadmium toxicity and tolerance in plants. Narosa Publishing House, New Delhi, pp 63–86

Shuman LM (1999) Effect of organic waste amendments on zinc adsorption by two soils. Soil Sci 164:197–205

Sinha S, Gupta AK, Bhatt K, Pandey K, Rai UN, Singh KP (2006) Distribution of metals in the edible plants grown at Jajmau, Kanpur (India) receiving treated tannery wastewater: relation with physico-chemical properties of the soil. Environ Monit Assess 115:1–22

Sipter E, Rozsa E, Gruiz K, Tatrai E, Morvai V (2008) Site-specific risk assessment in contaminated vegetable gardens. Chemosphere 71:1301–1307

Soumare M, Tack FMG, Verloo MG (2003) Characterisation of Malian and Belgian solid waste composts with respect to fertility and suitability for land application. Waste Manag 23:517–522

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. 2nd edn. John Wiley and Sons, New York

Strawn DG, Sparks DL (2000) Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci Soc Am J 64:144-156

TERA (Toxicology Excellence for Risk Assessment) (2010) International toxicity estimates for risk (ITER) database. http://www.tera.org/iter. Accessed 13 August 2010

Unsal T, Ok SS (2001) Description of characteristics of humic substances from different waste materials. Bioresour Technol 78:239–242

US EPA (United States Environmental Protection Agency) (2005) Test methods for evaluating solid waste, physical/chemical methods, series 3000. http://www.epa.gov/epaoswer/hazwaste/test/main.htm/. Accessed 27 October 2008.

Walker DJ, Clemente R, Bernal MP (2004) Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chemopdium album* L. in a soil contaminated with pyritic mine waste. Chemosphere 57 :215-224

Walter I, Martinez F, Cuevas G (2006) Plant and soil responses to the application of composted MSW in a degraded, semiarid shrubland in central Spain. Compost Sci Util 14:147–154

Warman PR, Rodd V (1998) Influence of source-separated MSW compost on vegetable crop growth and soil properties: year 3. In: Proceedings of the 8th Annual Meeting of the Composting Council of Canada, Ottawa, Ontario. pp 263–273

Weng L, Fest Epm, Fillius J, Temminghoff Ejm, van Riemsdijk Wh (2002) Transport of humic and fulvic acids in relation to metal mobility in a copper-contaminated acid sandy soil. Environ Sci Technol 36:1699–1704

Table 1 Summary of analyses (mean ± S.D.) of standard reference materials (SRM): NIST 2711 Montana soil and NIST 1573a tomato leaves. In each case, 3 replicate samples were analyzed. NC = NIST 1573a was not certified for Pb.

SRM	Metal	Detection limit (mg l^{-1})	Distilled water blank (mg l^{-1})	Reagent blank (mg l^{-1})	Measured value (mg kg^{-1})	Certified value (mg kg^{-1})	% NIST metal measured
Montana soil	Cd	0.0010	0.0011 ± 0.0001	0.0067 ± 0.0006	40.5 ± 1.3	41.70 ± 0.25	97.7 ± 3.7
	Cu	0.0015	0.0010 ± 0.0001	0.0027 ± 0.0003	110.2 ± 5.0	114 ± 2	96.7 ± 6.1
	Pb	0.0045	0.0012 ± 0.0000	0.015 ± 0.001	1051.9 ± 31.4	1162 ± 31	90.5 ± 5.1
	Zn	0.0010	0.0013 ± 0.0002	0.038 ± 0.001	314.9 ± 9.3	350.4 ± 4.8	89.9 ± 3.9
Tomato leaves	Cd	0.0010	0.0002 ± 0.0000	0.0013 ± 0.0006	1.50 ± 0.09	1.52 ± 0.04	98.7 ± 8.5
	Cu	0.0015	0.0007 ± 0.0000	0.0027 ± 0.0015	4.62 ± 0.28	4.70 ± 0.14	98.3 ± 8.9
	Pb	0.0045	0.0010 ± 0.0001	0.0023 ± 0.0006	0.25 ± 0.25	NC	NC
	Zn	0.0010	0.0009 ± 0.0001	0.0047 ± 0.0006	29.9 ± 0.6	30.9 ± 0.7	96.8 ± 4.1

Table 2 Physicochemical characteristics of the experimental soils and compost. Soil Type: W, Baldwin; D, Despina; S, St. Gerard; A, Blackfriar's A; B, Blackfriar's B; C, compost. Each soil was mixed with compost to yield 0, 9, or 25% compost in the experimental soils. OM is percentage organic matter (w/w). Each value is the mean ± SE of 3 replicates. * Values represent significant ($p<0.001$) differences within a column

		Physicochemical Soil Properties					
Soil	Compost %	OM %	Conductivity µS/cm	pH	Sand %	Silt %	Clay %
W	0	6.9 ± 0.4	406 ± 37	8.0 ± 0.0	87.6 ± 1.87	7.8 ± 0.6	4.6 ± 1.5
	9	7.5 ± 0.3	671 ± 18	7.8 ± 0.0	80.2 ± 4.61	19.7 ± 4.6	0 ± 0.0
	25	11.3 ± 0.3	535 ± 17	7.8 ± 0.0	66.8 ± 4.05	18.8 ± 0.8	14.3 ± 4.7
D	0	10.3 ± 0.2	548 ± 23	8.0 ± 0.0	61.5 ± 2.46	11.4 ± 2.6	27.3 ± 2.8
	9	9.1 ± 0.4	779 ± 48	7.8 ± 0.1	31.2 ± 3.0	56.9 ± 3.1	9.3 ± 3.1
	25	13.1 ± 0.3	642 ± 33	7.8 ± 0.0	60.3 ± 1.72	19.0 ± 4.5	20.6 ± 2.0
S	0	8.8 ± 0.8	457 ± 13	8.2 ± 0.0	66.9 ± 2.53	114.2 ± 0.3	18.8 ± 2.1
	9	10.1 ± 0.2	476 ± 14	7.7 ± 0.0	27.0 ± 2.01	42.8 ± 6.0	30.1 ± 2.2
	25	14.0 ± 0.5	777 ± 12	7.8 ± 0.0	38.4 ± 4.43	47.6 ± 1.7	14.1 ± 0.2
A	0	12.2 ± 1.3	543 ± 12	8.0 ± 0.0	84.3 ± 1.63	7.3 ± 2.3	8.4 ± 0.8
	9	13.4 ± 0.3	400 ± 43	7.8 ± 0.0	52.8 ± 3.08	43.2 ± 3.7	4 ± 0.0
	25	15.2 ± 0.5	559 ± 10	7.8 ± 0.0	49.9 ± 0.23	41.9 ± 1.4	8.2 ± 0.2
B	0	18.2 ± 3.4*	1330 ± 13*	8.2 ± 0.0	95.3 ± 4.0	4.7 ± 0.2	0 ± 0.0
	9	17.4 ± 0.4	631 ± 9	7.9 ± 0.0	75.3 ± 4.0	20.5 ± 4.2	4.2 ± 0.2
	25	18.5 ± 0.3*	769 ± 109	7.8 ± 0.1	58.2 ± 6.3	28.3 ± 1.3	13.4 ± 3.0
C	100	30.8 ± 1.9*	1018 ± 78*	7.3 ± 0.0*	69.1 ± 4.0	5.5 ± 1.5	25.2 ± 7.7

Table 3 Proportion of total (%) Cd, Cu, Pb, and Zn in the experimental soils present as the free metal ion or bound to fulvic and humic acids (FA and HA) as estimated using NICA-Donnan modeling in Visual MINTEQ. Only free metal ions are predicted to be bioavailable to plants. For the purposes of estimating bioavailability, metal ions loosely attracted to FA and HA were added to the free metal component. FA-metal and HA-metal represent covalent complexes, which are not believed to be bioavailable

Percentage of total metal in solution															
Soil	W			D			S			A			B		
Compost %	0	9	25	0	9	25	0	9	25	0	9	25	0	9	25
Cd															
Cd^{2+}	96.9	96.9	96.4	92.7	96.3	97.0	20.5	51.3	86.2	93.5	96.6	96.8	96.5	98.0	97.0
FA-Cd	1.8	2.0	2.3	4.4	2.3	2.1	26.1	23.6	9.3	3.9	2.3	2.1	2.4	1.7	2.2
HA-Cd	1.4	1.1	1.4	2.9	1.4	1.0	53.4	25.1	14.5	2.5	1.2	1.1	1.1	0.4	0.8
Cu															
Cu^{2+}	38.9	49.3	46.7	50.8	48.2	55.5	11.5	8.8	71.6	57.8	52.9	52.4	42.3	44.9	41.6
FA-Cu	16.7	17.5	17.7	16.4	18.2	18.5	25.0	30.8	9.2	13.2	17.7	17.7	25.0	36.1	28.5
HA-Cu	44.4	33.2	35.6	32.8	33.6	26.0	46.8	37.2	19.2	29.0	29.3	29.9	32.8	19.1	29.9
Pb															
Pb^{2+}	84.4	86.8	84.1	84.3	81.0	86.6	1.9	2.2	83.0	85.5	91.5	90.2	86.4	94.0	92.0
FA-Pb	4.2	4.4	4.9	6.9	8.3	6.0	61.6	69.1	7.6	4.6	3.4	3.7	5.5	4.0	3.9
HA-Pb	11.5	8.8	11.0	8.8	10.6	7.4	36.4	28.6	9.5	9.9	5.1	6.2	8.1	2.0	4.2
Zn															
Zn^{2+}	98.3	98.0	97.7	97.9	98.2	98.5	79.7	80.0	97.7	98.3	97.8	97.6	97.6	98.0	97.6
FA-Zn	0.01	0.02	0.02	0.02	0.02	0.02	0.31	0.45	0.02	0.01	0.02	0.02	0.03	0.05	0.03
FA-Zn	1.7	2.0	2.3	2.1	1.8	1.4	19.7	18.9	2.3	1.7	2.2	2.4	2.4	2.0	2.3

Table 4 Correlation coefficients between fulvic acid (FA) and humic acid (HA) concentrations in soils (mg/g) and the bioconcentration factors (BCF) of Cd, Cu, Pb, and Zn in green bean pods, lettuce leaves and carrot roots. Correlation coefficients between FA and HA and vegetable BCF were also calculated for soil S. Some correlations were not determined (nd) because the corresponding metal was below the detection limit in the plant tissue

Pearson Correlation Coefficients (all soils combined)						
	Green Bean		Lettuce		Carrot	
Metal	FA	HA	FA	HA	FA	HA
Cd	nd	nd	-0.44	-0.51*	nd	nd
Cu	0.26	0.53*	0.44	0.04	-0.03	0.39
Pb	0.15	0.34	0.04	0.28	nd	nd
Zn	0.46	0.17	0.52*	0.20	-0.12	0.43
Pearson Correlation Coefficients (soil S only)						
Cd	nd	nd	0.35	-0.55	nd	nd
Cu	0.73*	-0.31	0.28	-0.62	0.41*	0.47
Pb	0.29	-0.72	0.77*	-0.51	nd	nd
Zn	0.89*	-0.59	0.66*	-0.45	-0.18	-0.18

* Values are significant at $p < 0.05$

Figure Captions

Fig 1 Concentrations of Cd (a), Cu (b), Pb (c) and Zn (d) in the experimental soils and compost. Soil Type: W, Baldwin; D, Despina; S, St. Gerard; A, Blackfriar's A; B, Blackfriar's B; C, compost. Each value is the mean $\pm$ SE of 3 replicates. --- Denotes Canadian Soil Quality Guidelines (CCME 2006). * Denotes a significant difference ($p<0.05$) from unamended soil within each soil type

Fig 2 Concentrations of the dissolved soil organic carbon in the fulvic acid (FA) and humic acid (HA) fractions of the experimental soils and compost. Soil Type: W, Baldwin; D, Despina; S, St. Gerard; A, Blackfriar's A; B, Blackfriar's B; C, compost. Each value is the mean $\pm$ SE of 3 replicates. * Denotes a significant difference ($p<0.05$) from unamended soil within each soil type

Fig 3 Bioconcentration factors (BCFs) of green bean pods (a, d, g, j), lettuce leaves (b, e, h, k) and carrot root (c, f, i, l) grown in the experimental soils. $BCF=M_e/M_s$ (concentration of metal in the edible tissue/concentration of metal in the soil). Soil Type: W, Baldwin; D, Despina; S, St. Gerard; A, Blackfriar's A; B, Blackfriar's B; C, compost. 'bdl' indicates the metal concentration was below the detection limit. White boxes surrounding experimental soil labels indicate cases in which the BCF was higher in the 25% compost mixture compared to the unamended soil; grey boxes indicate a decrease in BCF with addition of 25% compost. Each value is the mean $\pm$ SE of 3 replicates. * Denotes a significant difference ($p<0.05$) from the unamended soil.

Fig 4 Hazard quotients (HQ) of green bean pods (a, d, g, j), lettuce leaves (b, e, h, k) and carrot root (c, f, i, l) grown in the experimental soils. HQ is an estimate of risk associated with consumption, with HQ>1 representing a potential health hazard. Soil Type: W, Baldwin; D, Despina; S, St. Gerard; A, Blackfriar's A; B, Blackfriar's B; C, compost. 'bdl' indicates the metal concentration was below the detection limit. --- Denotes HQ=1

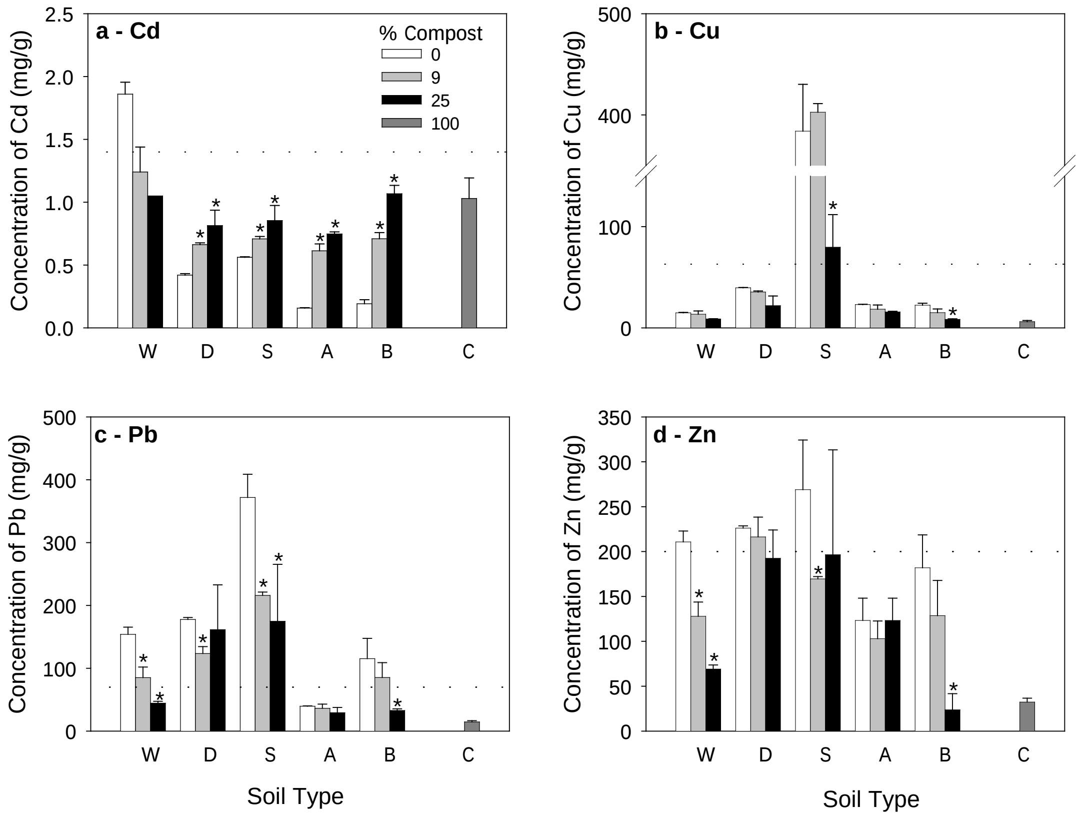

a - Cd
% Compost
0
9
25
100
Concentration of Cd (mg/g)
b - Cu
Concentration of Cu (mg/g)
c - Pb
Concentration of Pb (mg/g)
d - Zn
Concentration of Zn (mg/g)
W D S A B C
Soil Type

Fig. 1

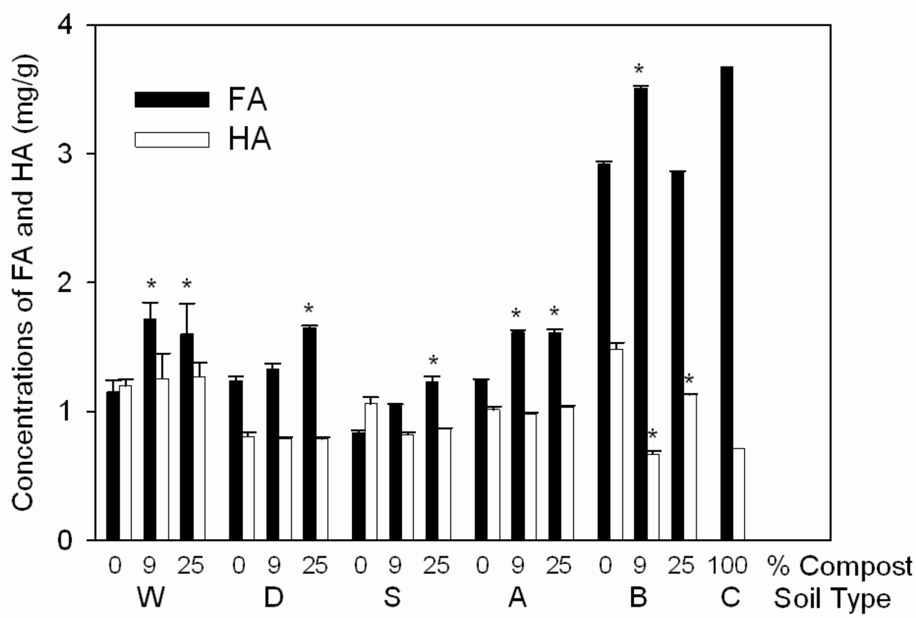
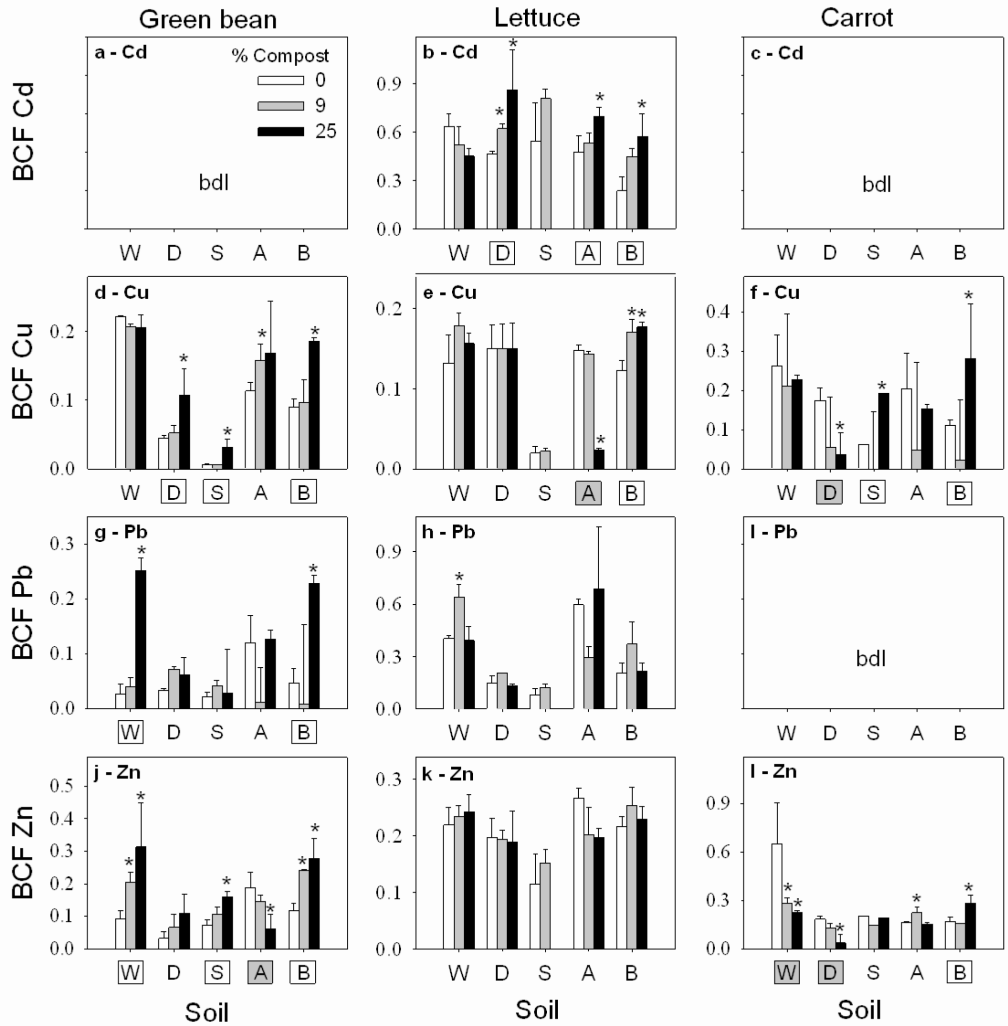

FA
HA
Concentrations of FA and HA (mg/g)
0
1
2
3
4
0 9 25 0 9 25 0 9 25 0 9 25 0 9 25 100 % Compost
W D S A B C Soil Type

Fig. 2



Green bean
Lettuce
Carrot
BCF Cd
BCF Cu
BCF Pb
BCF Zn
a - Cd
% Compost
0
9
25
bdl
b - Cd
c - Cd
bdl
d - Cu
e - Cu
f - Cu
g - Pb
h - Pb
i - Pb
bdl
j - Zn
k - Zn
l - Zn
W D S A B
Soil
Soil
Soil

Fig. 3

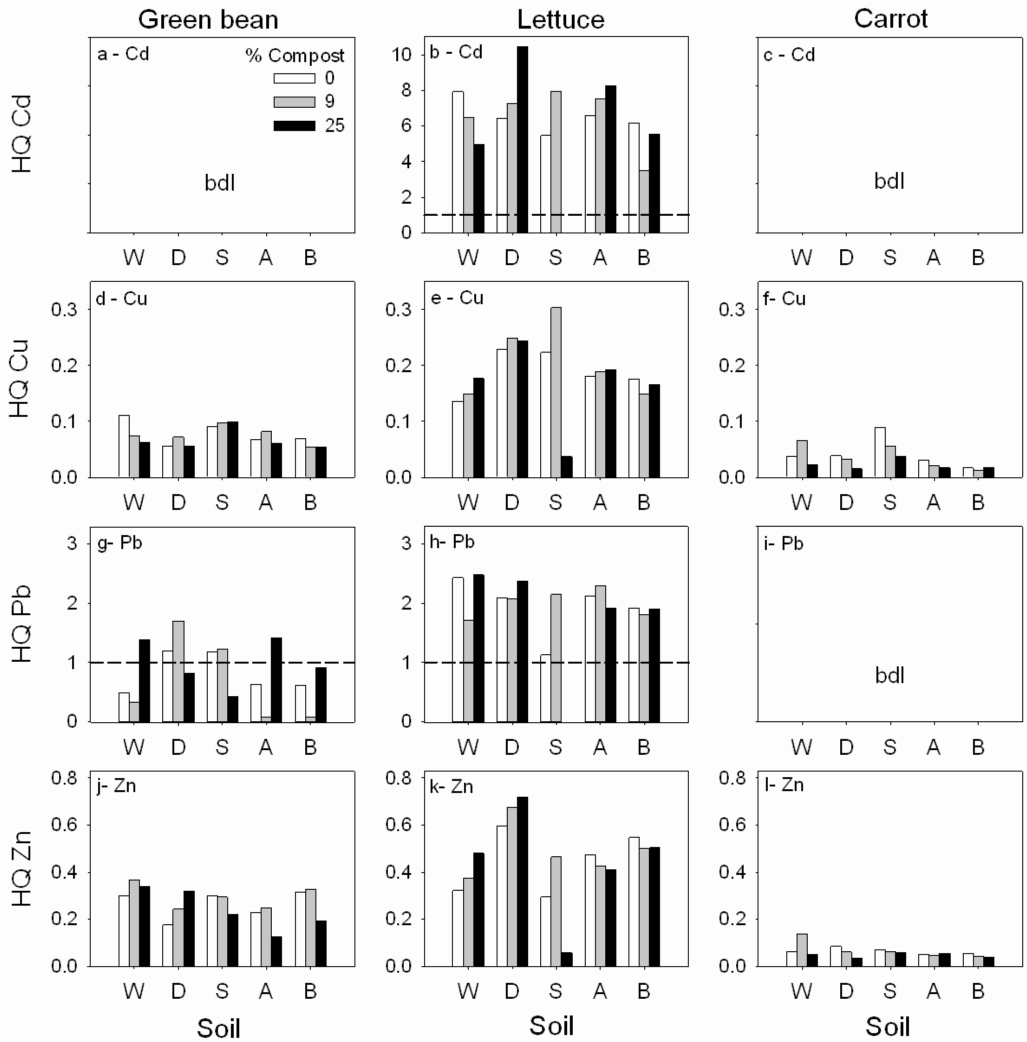

Green bean
Lettuce
Carrot
HQ Cd
HQ Cu
HQ Pb
HQ Zn
a - Cd
% Compost
0
9
25
bdl
b - Cd
c - Cd
bdl
d - Cu
e - Cu
f- Cu
g- Pb
h- Pb
i- Pb
bdl
j- Zn
k- Zn
l- Zn
W D S A B
Soil
Soil
Soil

Fig. 4