Chemosphere 112 (2014) 412–419

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Assessments of chromium (and other metals) in vegetables and potential bio-accumulations in humans living in areas affected by tannery wastes

Hualin Chen [a,*], Joselito M. Arocena [a,b], Jianbing Li [b], Ronald W. Thring [b], Jiangmin Zhou [a]

[a] College of Life and Environmental Sciences, Wenzhou University, Wenzhou 325035, PR China
[b] Environmental Science and Engineering Program, University of Northern British Columbia, Prince George, British Columbia V2N 4Z9, Canada

HIGHLIGHTS

- Bio-availability of metals to plants is metal, site and plant specific.
- Transfer functions are better than transfer factors to estimate Cr uptake.
- Potential Cr accumulations in humans is predictable from soil Cr bio-availability.

ARTICLE INFO

Article history:
Received 17 August 2013
Received in revised form 25 April 2014
Accepted 26 April 2014
Available online 28 May 2014

Handling Editor: A. Gies

Keywords:
Cd, Pb, Zn, Cu
Metal bio-availability
Transfer function
DTPA, EDTA

ABSTRACT

Chromium (Cr) commonly enters the food chain through uptake by vegetables. However, accurate prediction of plant uptake of Cr (and other metals) still remains a challenge. In this study, we evaluated 5 indices of availability for Cr (and other metals) to identify reliable predictors of metal transfer from soils to garlic, onion, bokchoy, radish and celery grown in soils impacted by tannery wastes. The potential bio-accumulation of Cr in humans was calculated from the Cr content of vegetable predicted by the best bio-availability index, amounts of vegetable consumed and recommended daily doses for Cr. Our results show that soil total Cr is the best predictor of Cr transfer from soils to onion (Cr in onion = 8.51 + 0.005 Total Cr) while Cr extractable by Synthetic Precipitation Leaching Procedure at pH 5 correlates very well with Cr uptake by bokchoy (Cr bokchoy = 5.86 + 7.32 SPLP-5 Cr) and garlic (Cr garlic = 7.63 + 2.36 SPLP-5 Cr). The uptake of Cr by radish and celery could not be reliably estimated by any of the 5 indices of availability tested in this study. Potential bio-accumulation of Cr in humans (BA-Cr) increases from soils with low Cr (BA-Cr = 11.5) to soil with high total Cr (BA-Cr = 31.3). Due to numerous soil factors affecting the behavior of Cr in soils and the physiological differences among vegetables, we suggest that the prediction of the transfer of Cr (and other metals) from soils to plants should be specific to site, metal and vegetable. Potential bio-accumulation of Cr in humans can be derived from a transfer function of Cr from soils to plants and the human consumption of vegetables.

1. Introduction

Leather tanning processes are known to release high amounts of metals such as chromium (Cr) into the environment. Improper disposal of sludge and wastewater generated from leather factories in Shuitou, China has impacted nearby alluvial soils with as high as 2484 mg kg^{-1} Cr (Chen et al., 2012). The fate of Cr in soils and the environment is of concern particularly the carcinogenic and mutagenic properties of Cr(VI) (Adriano, 2001; Avudainayagam et al., 2003; Shanker et al., 2005).

Abbreviations: BA, bio-accumulation; TDI, total daily intake; DTPA, diethlylenetriamine pentaacetic acid; EDTA, ethylenediamine tetraacetic acid; SPLP, Synthetic Precipitation Leaching Procedure; TA, threshold amount; TOT, total; TF, transfer factor; TFn, transfer function; M, mol/L.

[*] Corresponding author. Address: College of Life and Environmental Sciences, Wenzhou University, Wenzhou, Zhejiang Province 325035, PR China. Tel.: +86 577 8669 7847; fax: +86 577 8668 9257.

E-mail addresses: hualin2100@126.com (H. Chen), Joselito.Arocena@unbc.ca (J.M. Arocena), Jianbing.Li@unbc.ca (J. Li), Ron.Thring@unbc.ca (R.W. Thring), rosechl@163.com (J. Zhou).

http://dx.doi.org/10.1016/j.chemosphere.2014.04.091
0045-6535/

One common pathway of Cr entry from soils to the food chain is through consumption of Cr-enriched vegetables especially those grown in soils impacted by tannery wastes. Carriers of essential anion (e.g., SO_4^{2-}) transport CrO_4^{2-} from soil to plants because of structural similarities (Cervantes et al., 2001; Kaszycki et al., 2005; Shanker et al., 2005). Chromium is also passively taken up by plants as Cr(III) (Shanker et al., 2005) although higher uptake was observed in most plants grown in Cr(VI) than Cr(III) (Zayed et al., 1998). Once absorbed in plants, Cr is solely stored as Cr(III) in roots and leaves of 12 vegetables supplied with both Cr(VI) and Cr(III) as revealed using X-ray absorption analysis (e.g., Zayed et al., 1998; Bluskov et al., 2005). Among 15 plants grown in metal-contaminated soils in India, it has been reported that tomato (*Lycopersicon esculentum*) absorbs the highest amount of Cr (108 mg kg^{-1} Cr) while sponge gourd (*Luffa aegyptiaca* Mill.) has the lowest Cr uptake at 5.9 mg kg^{-1} Cr (Gupta and Sinha, 2006). Chromium is toxic to growth and development of plants at concentration >5.2 mg kg^{-1} Cr (Davies et al., 2002). However, some plants such as *Brassica juncea* can tolerate high concentrations of Cr because of their ability to sequester Cr in epidermal and cortical cells in the roots and epidermal and spongy mesophyll cells in leaves (Bluskov et al., 2005). Health risks associated with Cr-contaminated soils have been evaluated by comparison of the consumption of vegetables with known amounts of Cr with the allowable total daily intake for Cr (e.g., Gupta and Sinha, 2006; Maleki and Zarasvand, 2008). If uptake of Cr by plants can be accurately predicted, then risk assessment associated with Cr-contaminated soils will be highly successful (Jamali et al., 2007). Prediction of potential transfer of Cr (and other metals) to plants is primarily based on bio-available Cr species estimated from extractants such as diethlylenetriamine pentaacetic acid (DTPA) and ethylenediamine tetraacetic acid (EDTA) (Lindsay and Norvell, 1978; Ure et al., 1993; Quevauviller et al., 1998; Jamali et al., 2007; Gupta and Sinha, 2007a). Jamali et al. (2007) predicted the transfer of Cr from contaminated soil to plants by the ratio of Cr in plants to Cr in soils extracted by 0.05 M EDTA. In our previous report (Chen et al., 2012), we used the Synthetic Precipitation Leaching Procedure (SPLP), Method 1312 (USEPA, 1994) to assess the leachability of Cr (and other metals) based on an assumption that SPLP is a measure of the pore-water chemistry of soils (Townsend et al., 2006). Among others, US EPA Method 1312 determines the mobility of inorganic analytes in soils. If the SPLP solution truly represents soil solution composition, then it can be used to evaluate the potential amounts of bio-available Cr and other metals because plant roots primarily absorb nutrients from soil solution (McBride, 1994). Wolt (1994) suggested that soil solution provides one of the most important indices of nutrient bio-availability to plants. Although not reported for Cr(VI) or Cr(III) yet, the use of diffusive gradient in thin films has been suggested to provide a good measure of bio-available metals (e.g., Collins and Kinsela, 2011). Similarly and to our knowledge, the correlation between soluble Cr(VI) extracted by alkaline extractant at pH 7.2 (e.g., James and Bartlett, 1983) has yet to be reported in literature. However, water-soluble Cr(VI) is negatively correlated with dry matter yield of *B. juncea* (Bolan et al., 2003). The main objective of this paper was to understand the transport of Cr and other metals (Cd, Cu, Pb and Zn) from soils into vegetables and other crops grown in metal-polluted soils. Specifically, we (1) determined 5 indices of metal availability in soils, (2) measured the uptake of Cr, Cd, Pb, Cu and Zn in 5 vegetables, and (3) identified the metal availability indices that best assessed the potential transfer of soil Cr (and other metals) into each experimental vegetable grown in soils impacted by Cr-containing wastes from leather tanneries. In addition, we evaluated the potential human health risks (or potential human bio-accumulation of Cr) associated with the customary consumption of vegetables grown by local inhabitants in the study areas.

2. Materials and methods

2.1. Study area

The study area was located on the flood plains of the Aojiang river at Shuitou town, Pingyang county, Zhejiang province, People's Republic of China. The leather tanning industry in the area started in the late 1980s and peaked in the early 2000s with an estimated generation of up to 9500 tons of Cr-containing wastes every year (Chen et al., 2012). Soils on the flood plains in the study area are inherently fertile due to frequent floods and are currently planted with a variety of vegetables for family consumption and/or as sources of additional income. Selected properties of soils in the study area have the following range of values: pH 5.8–7.5, total C (%) 1.7–1.9, total N (%) 0.11–0.15, total Ca (%) 0.4–1.0, total Fe (%) 2.9–3.2 and total Al (%) 4.9–9.3 (Chen et al., 2012).

2.2. Total and bio-available Cr, Cd, Pb, Cu and Zn in soils

Eighteen soil samples were collected from 3 sites (Shuitou-1, Shuitou-2 and Shuitou-3) to represent different amounts of soil total Cr in the study area. Initial samples from these distinct sites have an increasing soil total Cr contents (mean and standard error) from 139 (71) to 359 (101) to 1350 (416) mg kg^{-1} Cr, respectively for Shuitou-1, -2 and -3 (Chen et al., 2012). Total metal contents were analyzed using HF and microwave digestion method (USEPA, 1996). We used reference samples of EnviroMAT Contaminated Soil SS-1 and SS-2 as quality control samples. Bio-available metals were estimated using the conventional DTPA and EDTA extractions (Quevauviller et al., 1998). Briefly, 50 mL of 0.05 M EDTA was added to 5 g soil sample while DTPA extraction was carried out using 10 g soil sample and 20 mL of 0.005 M DTPA solution. The mixtures were shaken at 30 rpm in an end-over-end shaker at 20 °C for 1 and 2 h, respectively for EDTA and DTPA techniques (Quevauviller et al., 1998). The amounts of extracted Cr, Cd, Pb, Cu and Zn in the extracts were determined by using atomic absorption spectrometry (AA800, PerkinElmer). We also considered the amounts of Cr, Cd, Pb, Cu and Zn extracted by the SPLP method (USEPA, 1994) at pH 4.2 and 5.0 as measures of bio-available metals. In brief, we mixed 100 mL of leaching solution (i.e., a 40:60 HNO_3:H_2SO_4 at pH 5.0 ± 0.05 or 4.2 ± 0.05) to a 5.0-g sample in a glass jar. The 1:20 soil:solution mixture was gently shaken on a horizontal shaker for 18 h and then allowed to settle for 30 min prior to the pH determination of the supernatant. The extract was filtered using a 0.45-μm fiber glass filter. The filtrate was acidified to $pH < 2.0$ with concentrated HNO_3 prior to the determination of Cr, Cd, Cu, Pb and Zn using atomic absorption spectrometry (AA800, PerkinElmer).

2.3. Collection, preparation and chemical analysis of vegetable samples

A total of 41 composite samples of 5 commonly-grown vegetables in the study area were collected for this study: garlic (*Allium sativum* L.), Chinese cabbage or bokchoy *(Brassica chinensis* L.*)*, onion *(Allium cepa* L.*)*, radish *(Raphanus sativus* L.*)* and celery *(Apium graveolens* L.*)*. If available, one sample of each vegetable was uprooted from 3 random locations in each of the 3 sites in the study area. Samples of carrot (*Daucus carota* L. var. *sativa* Hoffm), cilantro *(Coriandrum sativum* L.) and pea *(Pisum sativum* L.) were also collected and analyzed for uptake of Cr (and other metals) but were excluded from this manuscript because these vegetables were not grown in all three sites.