Bull. Environ. Contam. Toxicol. (2006) 77:658–664

DOI: 10.1007/s00128-006-1113-9

Bulletin of Environmental Contamination and Toxicology

Chromium Levels in Vegetables and Grains Grown on Tannery Effluent Irrigated Area of Jajmau, Kanpur, India: Influence on Dietary Intake

A. K. Gupta, S. Sinha

Ecotoxicology and Bioremediation, National Botanical Research Institute, Rana Pratap Marg, Post Box Number 436, Lucknow 226 001, India

Received: 6 June 2006/Accepted: 19 October 2006

The main source of chromium in natural soils is weathering of their parent materials and the average amount of Cr in various kinds of soils ranges from 0.02 to 58 μmol g^{-1} (Richard and Bourg 1991). An increase in total Cr concentration in agricultural soils originates from fallout and washout of atmospheric Cr containing particles as well as from the chrome bearing sludge and refuse from industrial activity. In the environment, chromium (III) and (VI) are most common and stable forms of the metal, however, the toxicity depends on its chemical form. Chromium (VI) compounds have a toxic, mutagenic and even carcinogenic nature, whereas, the trivalent forms, which prevails in foods has a low toxicity (Goyer 1995). It is an essential trace mineral nutrient for normal sugar and fat metabolism which functions primarily by potentiating the action of insulin.

India stands 10th in the world in its footwear production and is one of the highest producers of raw skins and hides. There are more than 2500 tanneries in the country and nearly 80% of the tanneries are engaged in the chrome tanning process. In Uttar Pradesh, Jajmau (Kanpur) is a prominent center for leather processing. There is a cluster of tannery industries (about 350) along the banks of river Ganga and about 75,000 tonnes of cow and buffalo hides are processed annually, which is 15% of the total quantity. These tanneries specialize in processing hides into heavy leather (sole, harness and industrial leather). This is the only center in India, where saddlery products are manufactured. The wastewater discharged from these industries contains high concentration of Cr (Ramasami 1999).

Vegetables constitute essential components of the diet by contributing protein, vitamins, iron, calcium and other nutrients. It can take up high amount of essential and toxic metals from contaminated sites (soils/ water). The essential metals are required for the growth of the plant in small quantities and the presence of excessive concentration may cause toxicity. Furthermore, the physical and chemical forms of metals in which they are dispersed, may increase the metal availability in vegetables. The uptake of Cr from the agricultural soils depends on their solubility, soil pH, organic matter, plant species, fertilizer and soil type. The accumulation of metals including Cr in the edible parts of the plant grown in agricultural soil contaminated with industrial wastewater has been well documented (Smith et al. 1996; Barman et al. 2000; Sinha et al. 2005, Sinha et al. 2006). The total metal content was reported in the soil which does not necessarily provide an accurate guide to the amount of metal bioavailable to the plants and ultimately to the food-chain (Rieuwerts et al. 1998). Further, it has been reported that the accumulation of metals in the plants depends on

Correspondence to: S. Sinha

DTPA extractable metals (Soltanpour 1991). The purpose of the study was, thus, to determine the concentration of chromium in the vegetables and crops grown in upflow anaerobic sludge blanket (UASB) treated tannery wastewater receiving areas of Jajmau, Kanpur and to estimate their contribution to the daily intake of the Cr in local population.

MATERIALS AND METHODS

Composite samples of vegetables (bottle gourd, cucumber, elephant's ear, tomato, potato, sponge gourd, cabbage, kidney bean, okra, long melon, chilli, spinach and egg plant) grains (rice and wheat) were collected from eight selected sites (S 1- S 8) during the two harvest periods, autumn 2002 and spring 2003. Composite soil samples from the root zone of the plants were collected. After harvesting, the edible portions of vegetables were carefully rinsed with tap and distilled water to remove surface contamination. The leafy stalks were removed from all the samples and these were sliced and dried on a sheet of paper to eliminate excess moisture. Once dried, each sample was oven dried at 60^0 C to constant weight. Each oven-dried sample was ground. The samples then stored in a clean dry, stopper glass container before analysis.

After dry weight determination, the samples were digested in HNO_3 (70%) using Microwave Digestion System MDS 2000 and chromium content was estimated using Atomic Absorption Spectrophotometer (GBC Avanta $\sum$). Chromium atomization was performed at a wavelength of 357.9 nm. The metal concentration was measured in triplicate for each sample. Prior to using the linear calibration method we checked that there were no matrix interferences after applying the Cr standard addition method to several samples.

The environmental exposure risk to the populations due to the intake of elevated levels of Cr from vegetables and crops grown in UASB treated tannery receiving wastewater areas over those unexposed ones has been evaluated by first computing the mean estimated total daily intake (TDI) of the metal using the equation :

$$\text{TDI (mg/ day)} = \Sigma\, Ci\, Di$$

Where, Ci is the mean concentrations of individual metal in the i^{th} media and Di is the mean daily intake of the vegetables by a person which was based on the survey of the village. The major intake routes considered are food grains (600 g/d) and vegetables (300 g/d).

The computed TDI (mg/d) values for each toxicant are then compared with their respective acceptable daily intake (ADI) values (mg/d), worked out from their individual ADIs (mg/d/kg bw) is available in the literature for a person of 60 kg body weight. The risk quotient (RQ) for Cr was computed using equation:

$$\text{RQ} = \text{TDI/ADI}$$

The standard reference material of metals (E-Merck, Germany) was used for calibration and quality assurance for each analytical batch. The reference solution of single element was used for calibration of analytical equipment and validation of test methods provided by National Physical Laboratory (NPL), New Delhi and their certified and observed values are given in Table 2.

RESULTS AND DISCUSSION

The results of the physico-chemical analysis of the UASB treated tannery effluent

Table 1. Accumulation (mg kg^{-1}) of chromium in the edibles parts of the vegetable/ grain samples collected from selected effluent irrigated sites of Jajmau (Kanpur).

English names	Botanical names	N*	Families
Bottle Gourd	*Lagernaria siceraria* (Molina) Standley	5	Cucurbitaceae
Cucumber	*Cucumis sativus* L.	6	Cucurbitaceae
Elephant's Ear	*Colocasia antiquorum*	4	
Tomato	*Lycopersicon esculentum*	4	Solanaceae
Potato	*Solanum tuberosum* L.	7	Solanaceae
Sponge gourd	*Luffa aegyptiaca* Mill.	7	Cucurbitaceae
Cabbage	*Brassica oleracea* var. *capitata*	6	Cruciferae
Kidney bean	*Phaseolus vulgaris* L.	8	Papilionaceae
Okra	*Abelmoschus esculentus* (L.)	6	Malvaceae
Long melon	*Cucumis melo* var. *utilissimus*	4	Cucurbitaceae
Chilli	*Capsicum frutescens* L.	5	Solanaceae
Spinach	*Spinacia oleracea* L.	6	Chenopodiaceae
Egg plant	*Solanum melongena* L	4	Solanaceae
Rice	*Oryza sativa* L.	7	Gramineae
Wheat	*Triticum aestivum* L.	7	Gramineae

N* = Occurrence sites

Table 2. Observed and certified values of chromium in ($\mu g\ ml^{-1}$).

Code No. (Cr)	Certified value	Observed value[a]	Accuracy (%)	R.S.D (%)
BND 402.02	2.00±0.02	1.98±0.03	99.00	1.51

[a] Mean ± S.D. (n = 10)

which is being used for the irrigation of agricultural land at Jajmau (Kanpur) showed high levels of pH (7.26), EC (8.11dSm^{-1}), BOD (273 mg l^{-1}), COD (1360 mg l^{-1}). The level of Cr was found high in treated effluent (3.20 g ml^{-1}).

The data of diethylene triamine penta acetic acid (DTPA) extractable Cr from the agricultural soil at selected sites was represented in Figure 1. The analysis of the results showed maximum (24.26 mg kg^{-1} dw) amount of DTPA extractable Cr at S-5 followed by S-7, i.e., 21.81 mg kg^{-1} dw. The lowest Cr concentration was found at site S-1 (13.26 mg kg^{-1} dw). The mean value of Cr from all the selected sites (S-1 to S-8) was calculated as 17.87 mg kg^{-1} dw. The variation in the metal contents observed in the vegetable and grain samples depends on physical and chemical nature of the soil and absorption capacity of metal by the plants, which is altered by innumerable environmental factor and nature of the plants.

Taking into account the concentration of Cr in food samples (Table 3), their contribution to the mean daily intake by adult inhabitants at Jajmau, Kanpur was calculated by multiplying the mean Cr content of vegetables and grains by its mean consumption at Jajmau, Kanpur per person per day. On the basis of the results obtained, the daily dietary intake of total chromium for every group of vegetables and grains were estimated which was found minimum (1.78 mg d^{-1}) for sponge gourd and maximum (32.47 mg d^{-1}) for tomato.

Singh et al. (2004) reported the impact of metals and pesticides in all the environmental

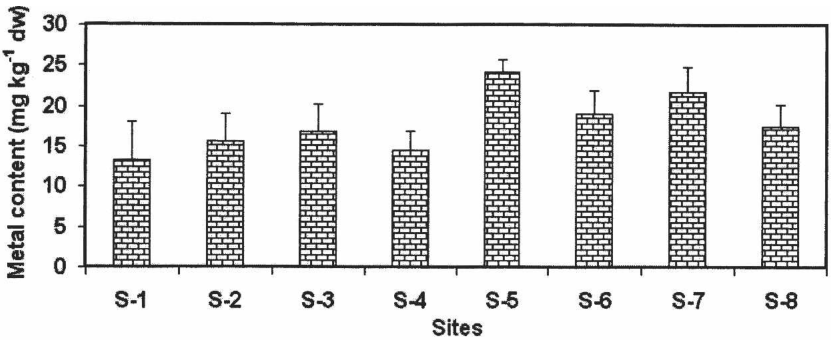

Figure 1. DTPA extractable Cr in the soil samples collected from different sites of Jajmau, Kanpur

media, suggesting a definite adverse impact on the environmental quality of Kanpur (India). The levels of metals were recorded high in the samples of human blood and urine of the different population groups. The major intake routes considered are drinking water, food grains, vegetables and milk, which contain high level of metals. These authors also reported considerable risk and impact of the metals on the human health in the exposed area receiving wastewater. Further, risk quotient (RQ) was also evaluated and the values were 2-4 times higher over their respective unexposed population groups. Farooq et al. (1999) reported the accumulation of metals in the vegetables collected from dry bed River in the city of Kanpur and found more accumulation in leafy vegetables than fruit bearing vegetables, however, no such trend was recorded in the present study. Barman et al. (2000) studied the accumulation of metals in the economically important crops and vegetables irrigated with the water of loamy drain which receives tannery wastewater after treatment at CETP (common effluent treatment plant), Unnao (Uttar Pradesh) India. They have reported that the accumulation of toxic metal (Cr) in the fruit part of wheat was 8 $\mu g\ g^{-1}$ dw. In the present study, the mean value of Cr in the wheat grain (33.29 mg kg^{-1}) was found much higher which is due to high level of plant available Cr in the soil at Jajmau (Kanpur) at different sites. Recently, Sinha et al. (2006) also reported similar findings from Cr contaminated area. Parveen et al. (2003) purchased the samples (20 nos.) of food and vegetables from local market of Karachi (Pakistan) to assess the level of metals in edible parts of these plants. Out of all the samples, lowest level of Cr (0.15 ppm) was found in potato. Whereas, the edible parts of chillies, cucumber, tomato has shown high level of Cr in edible parts. In contrast, Santos et al. (2004) collected the samples from food distribution centers to assess the level of metals in the vegetables, derived products and animal products which are most frequently consumed by adult inhabitants of Rio de Janeiro city (Brazil). They reported that the recommended values of daily intake of Cr are lower than recommended daily allowance. Lendinez et al. (2001) also reported Cr content in cereals and vegetables which ranged from 0.007 to 0.456 $\mu g\ g^{-1}$ fresh weight.

The value TDI was calculated for selected vegetables and grains (Table 3). The analysis of the results showed that TDI value of wheat (19.97 mg d^{-1}) and rice (25.84 mg d^{-1}) was found almost equal. The TDI value of all the vegetables was found below 12 mg d^{-1} except bottle gourd (7.29 mg d^{-1}) and tomato (32.47 mg d^{-1}). Garcia et al. (2000) also reported that the dietary intake of Cr in spanish diet (0.41 μg /day) and accumulation

Table 3 Accumulation of Cr (mg kg^{-1}) in edible part of different plants collected from Jajmau, Kanpur.

English names	Cr* (mg kg^{-1})	TDI (mg d^{-1}) (300 g)	RQ (TDI/ADI)
Bottle Gourd	57.6±7.4	17.29	352.86
Cucumber	17.6±0.5	5.27	107.55
Elephant's Ear	29.8±8.9	8.94	182.45
Tomato	108.2±0.8	32.47	662.65
Potato	11.8±1.1	3.54	72.24
Sponge gourd	5.9±1.1	1.78	36.33
Cabbage	40.5±0.8	12.11	247.14
Kidney bean	19.4±1.7	5.83	118.98
Okra	6.7±1.6	2.02	41.22
Long melon	17.9±2.6	5.38	109.79
Chilli	10.2±1.9	3.07	62.65
Spinach	30.4±1.8	9.11	185.92
Egg plant	19.4±1.7	5.83	118.98
Rice	43.07±2.65	25.842	527.39
Wheat	33.29±2.60	19.974	407.63

*Mean of total occurrences. ADI = 0.049 mg d^{-1} (bw = 60 kg)

of Cr in spices and aromatic herbs is higher than the other food and beverages. In the present study, the daily intake of Cr was found higher than recommended by the US

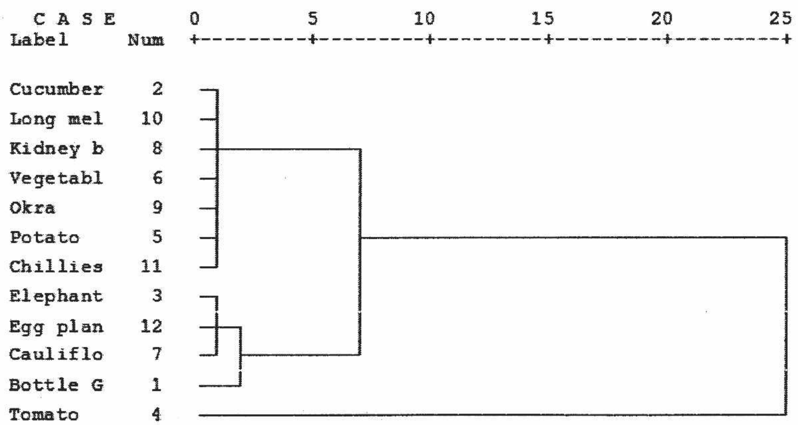

Figure 2. Dendrogram of hierarchical cluster analysis between different vegetables grown at Jajmau, Kanpur

National Council (NRC, 1989) for Cr (III) (0.05 to 0.2 mg). Further, the values of the present study fall in the high range (0.013-0.085 mg d^{-1}) than reported in the literature (Anderson et al. 1993; Dang 1998; FAA 2004). In present set of conditions, tomato is the biggest contributor for Cr intake followed by rice and wheat. Although, there is no reference nutrient intake (RNI) for Cr, a safe and adequate intake is believed to be above 25 μg /day for adults and between 0.1 and 1.0 μg kg^{-1} body weight per day for children and adolescence (Department of Health 1991).

Maximum risk quotient of Cr was calculated for tomato (662.65) followed by rice (527.39) and wheat (407.63) while, minimum 36.33 was recorded for sponge gourd. The results of cluster analysis (Figure 2) also conform to these results. It is recommended from the above analysis that farmers should not grow vegetables/grains having high risk quotient value calculated under present set of conditions.

These findings are important in view of high accumulation of Cr in edible parts of the plants grown in UASB treated tannery wastewater irrigated areas, however, the situation may change in future depending on the volume of contaminants added to the ecosystem. Thus, it is advisable that the edible plants grown on such area should be monitored periodically before consumption of the edible part. It may be concluded that the vegetables and crops growing in such contaminated area constitute high RQ due to accumulation of toxic metal, chromium.

Acknowledgments. We thank the Director, National Botanical Research Institute, Lucknow (India) for providing required research facilities and keen interest in the work. Dr.A.K Gupta is grateful to NRCD, Ministry of Environment and Forests, Govt. of India, New Delhi for financial assistance.

REFERENCES

Anderson RA, Bryden NA, Polonsky MM (1993) Dietary intake of calcium, chromium, copper, iron, magnesium, manganese and zinc: duplicate plate values corrected using derived nutrient intake. J American Diet Assoc 93 : 462-464

Barman SC, Sahu RK, Bhargava SK, Chatterjee C (2000) Distribution of heavy metals in wheat, mustard, and weed grown in field irrigation with industrial effluents. Bull Environ Contam Toxicol 64: 489-496

Dang HS, (1998) Daily dietary intake. Vienna: International Atomic Energy Agency (IAEA-TECDOC-1005)

Department of Health (1991) Dietary Reference Values for Food Energy and Nutrient for the United Kingdom. Report on Health and Social Subject: 41 The stationary office, London, UK

Farooq M, Hans RK, Viswanathan PN, Joshi PC (1999) Health hazard from dry river bed agriculture. Bull Environ Contam Toxicol 62: 555-562

FAA Medical virtual flight surgeons Aviation Vitamine Mineral Nutrition Supplen. Web-site Available at http:// www.aviationmedicine.com/vitamins.htm (Accessed on 28 Nov, 2004)

Garcia E, Cabrera C, Lorenzo ML, Lopez MC (2000) Chromium level in spices and aromatic herbs. Sci Total Environ 247: 51-56

Goyer RA, Cherion MG (1995) Toxicology of metals, biochemical aspects. Springer Verlag, Berlin, DM 498. Handbook of Experimental Pharmacology vol. 115. General Pharmacology: The Vascular System, Volume 27(4), June 1996, pp 743

Lendinez E, Lorenzo ML, Cabrera C, Lopez, MC (2001) Chromium in basic foods of the Spanish diet: seafood, cereals, vegetables, olive oils and dairy products. Sci Total Environ 278: 183-189

Parveen Z, Khuhro MI, Rafiq N (2003) Market Basket Survey for lead, cadmium, copper, chromium, nickle, and zinc in fruits and vegetables. Bull Environ Contam Toxicol 71: 1260-1264

Ramasami T, Rao JR, Chandrababu NK, Parthasaeathi K, Rao PG, Saravanan P, Gayatri R, Sreeram KJ (1999) Beamhouse and tanning operations: Process chemistry revisited. J Soc Leather Technol Chem 83 : 39-45

Richard FC, Bourg ACM (1991) Aqueous geochemistry of chromium: a review. Water Res 25: 807-816

Rieuwerts JS, Thornton I, Farago ME, Ashmore MR (1998) Factor influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chem Speciation Bioavail 10: 61-75

NRC (1989) Recommended Dietary Allowances, National Research Council (US) Sub-committee. Washington, DC: National Academy Press, pp.241

Santos EE, Lauria DC, Porto da Silveria C (2004) Assessment of daily intake of trace elements due to consumption of foddstuffs by adults inhabitants of Rio de Janerio city. Sci Total Environ 327: 69-79

Singh KP, Mohan D, Sinha S, Dalwani R (2004) Impact Assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health agricultural and environmental quality in the wastewater disposal area. Chemosphere 55 : 227-255

Sinha S, Pandey K, Gupta AK, Bhatt K (2005) Accumulation of metals in vegetables and crops grown in the area irrigated with river water. Bull Environ Contam Toxicol 74 : 210-218

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.

Smith CJ, Hopmans P, Cook FJ (1996) Accumulation of Cr, Pb, Cu, Ni, Zn And Cd In Soil Following irrigation with treated urban effluent in Australia. Environ Pollut 94: 317-323

Soltanpour PN (1991) Determination of nutrient availability and elemental toxicity by AB-DTPA soil test and ICPs. Adv Soil Sci 16: 165-189