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Assessing The Health Risk of Some Trace Metals Contents in Vegetables Sold in Local Markets of Tehran-Iran

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ABSTRACT: Contaminations of vegetables from local markets in Tehran city with lead, cadmium, chromium, copper and zinc; the subsequent human exposure risks were determined. Atomic Absorption Spectrophotometer (wet digestion) was used for the analysis. In four months of four seasons, May, August, November 2011 and February 2012, thirteen vegetable forms and crops were purchased randomly from local markets in Tehran, Iran. The concentrations of metals (mg/kg dry weight) in vegetable ranged from 0.9-9.3 for Pb, 1.0-2.1 for Cd, 0.11-12.11 for Cr, 11.1-59.1 for Cu and 41.51-1070 for Zn,. The results of the study indicated that lead, cadmium, chromium were present at concentrations above the permissible levels in vegetables, while the copper were present at levels below the permissible levels. The present study showed that the contributions of these vegetables to daily intake of Pb, Cd, Cr, Cu and Zn were 21.7%, 42.5%, 161.7%, 8.3% and 6.4% of PTDIs, respectively. It can be suggested that the consumption of these contaminated vegetables does not pose a health risk for the consumers as the values obtained are below the FAO/WHO limits, but the vegetables is not alone source of dietary heavy metals. Therefore, certain group of consumer such as elderly with cardiovascular problems and kidney deficiency who may intake these food items for long term should be extra cautions as they are more susceptible to toxicities.

Keywords**:** Heavy metals, Vegetables, Risk assessment, Daily intake, Iran

INTRODUCTION

Heavy metal contamination of the food items is one of the most important aspects of food quality assurance (Marshall 2004; Wang et al., 2005; Radwan and Salama 2006; Khan et al., 2008). Due to increased awareness of the risk these metals pose to food chain contamination, international and national regulations on food quality have lowered the maximum permissible levels of toxic metals in food items (Radwan and Salama 2006) .Vegetables as rich sources of vitamins, minerals, and fibers, and also have beneficial antioxidative effects, their consumption is increasing gradually, particularly among the urban community. However, intake of heavy metal-contaminated vegetables may pose a risk to the human health. Heavy metals are natural components of the Earth's crust that main rout enter to the human body is through Food (Ganjavi 2010). Some of these elements are essential for human health such as Cu, Fe, Mn, Zn while others, if present even at low levels and tendency to accumulate in human organs can be toxic (e.g., Cd, Pb, Hg, As) (Soliman and Zikovsky 1999 ; Onianwa et al., 1999; Viqar and Ahmed 1992) . The so-called essential metals can be toxic depending on their concentrations and speciation (e.g., Copper is relatively toxic for humans that in low concentration is essential but at higher concentration is toxic, Cr (III) is essential while at high concentration and particularly Cr (VI) is toxic (ATSDR 2011). Prolonged accumulation of heavy metals through food source may lead to chronic effect in different organs such as kidney, liver, heart and nervous system of humans (WHO 1992; WHO 1995; Jarup 2003) . Contamination of vegetables with heavy metal may be due to irrigation with contaminated water, soil pollution, and the addition of fertilizers and metal based pesticides, industrial emissions, transportation, the harvesting process, storage and/or at the point of sale (Khan et al., 2008; Zhuang et al., 2009; Behbahaniniaand Mirbagheri 2008). Research findings show that at least 20 million hectare of land in North and South Africa, South America, Middle East, Southern Europe, South west America, Mexico and a significant part of Central and East Asia is irrigated with untreated sewage chiefly for cultivating vegetables (Carr 2005; Dayle 1998). Investigation of soil pollution levels in fields and farmlands in the country has reveal that the quantity of Cd and Pb in samples collected from contaminated areas in the provinces of Tehran, Guilan, Mazandaran, Zanjan, Esfehan (Kalantari et al., 2006; Charkhabi et al., 2008; Abdolhossein et al., 2010; Bigdeli and Seilsepour 2008). It has been reported that vegetables and water contamination to Pb and Cd around Gorgan city, Iran (Shahryari and Shehamat 2012) . A high level of Pb, Cd and Cr in various vegetables was shown in cultivated around Sanandaj City (Maleki and Zarasvand 2008). Accumulate metals at concentrations that are probably toxic to human health has been reported in Vegetables grown at environmentally contaminated sites in Shahre Rey (Bigdeli and Seilsepour 2008).

Vegetables are staple part of human meal taken as food especially in Iran, yet little information is available on the heavy metal content in vegetables in Iran. In view of the importance of the role that trace metals play in health status of the human body, the present study was initiated to investigate the levels of contamination with heavy metals and then determine and emphasis on the toxicological implications of heavy metal concentration in crops.

MATERIALS AND METHODS

In four months of four seasons, May, August, November 2011 and February 2012, thirteen vegetable forms and crops were purchased randomly from local markets in Tehran, Iran. Plant samples were immediately transferred to plastic bags.

For Lead, Cadmium, Chromium, Copper and Zinc analyses, vegetable and crop samples were washed with distilled water to eliminate suspended particles. The non-edible parts were removed from all samples and they were cleaned with deionized water repeatedly. These were later dried in an oven at 65ºC for about 2 days and were ground there using a Grinding mills until they could pass through a 60 mesh sieve. The samples were stored in clean, dry, high density polyethylene bottles of 100 ml capacity with screw caps. Bottles were prewashed with nitric acid, rinsed with de-ionized water, dried and tested for contamination by leaching with 5 %nitric acid. The bottles contained no metal liners that could contaminate the samples. Samples were precisely weighed (2 gram each) and ground in a mortar followed by wet digestion with HNO_3: $HClO_4$ (2:1) in a conical flask for 2-3 hours on a sand bath. Some 10 ml of HCl was added. Digested samples were filtered with 0.45 µm pore size cellulose nitrate membrane filter paper (Millipore) and the volume was increased to 100 ml with distilled water and bottles were stored until flame atomic absorption spectrophotometry was performed. The samples were analyzed by an atomic absorption spectrophotometer (ALPHA 4, Chem Tech Analytical, England) using an air-acetylene flame for the five heavy metals – Pb, Cd, Cr, Cu and Zn, using at least three standard solution for each metal. A certified standard reference material (Alpha – Line, Chem Tech Analytical, England) was used to ensure accuracy, and the analytical values were within the range of certified values. All recoveries of the metals studied were greater than 95%. Based on the average concentration and the average consumption of edible vegetables, estimates of the amount of each heavy metal consumed were calculated. The daily intake of heavy metals through the consumption of the vegetables tested was calculated according to the given equation:

Daily intake of heavy metals (µg/day) = [Daily vegetable consumption× vegetable heavy metal concentration]

Health risk assessment and daily (or weekly) intake of heavy metals through vegetables was made by comparing the concentration of the contaminants recorded with national and international safe limits. The percent contributions to dietary intake of heavy metals of the vegetables tested were calculated by dividing the daily consumption rates of the heavy metals with the values of provisional tolerable daily intake (FAO/WHO 1999).

RESULTS AND DISCUSSION

The mean concentrations of heavy metals found in crop samples are summarized in Table 1. The results show high levels of Pb, Cd and Cr in all vegetables studied.

In the present investigation, the value of Lead (Pb) ranges from 1.10 to 9.30 mg/kg DW in various vegetables. The highest mean level (9.30 mg/kg DW) of Pb was recorded in Cabbage, while minimum mean concentration (1.10 mg/kg DW) was registered in Beet Root. All the samples examined had lead concentration above the permissible limit by FAO/WHO (0.5 mg/kg) in the food.

Daily intake of metals (DIM) In order to observe the health risk of any pollutant, it is very important to estimate the level of exposure that it was estimated according to the average vegetable consumption for adults in Table 2. The estimated daily intake of Lead in this study ranged between 0.8 and 46.5 µg/day i.e. 0.37-21.73% of the Provisional Tolerable daily Intake (PTDI; 214 µg/day) (Table 2).

PTWI (the estimated weekly intake) of Lead ranged between 0.09 and 5.42 µg/kg-bw/week i.e. 0.4-22% of the Provisional Tolerable Weekly Intake, (PTWI; 25 µg/kg/bw/week) in this study.

The mean Cadmium (Cd) content varies from 1.02 to 2.09 mg/kg DW, mean Cd content was found high in Chinese Cabbage (2.09 mg/kg DW), while Aubergine showed low mean concentration of Cd (1.02 mg/kg DW). As table 1 show all the samples examined had cadmium concentration above the permissible limit by FAO/WHO (0.1mg/kg) in the food.

The estimated daily intake of Cd in this study ranged between 0.2 and 25.5 µg/day i.e. 0.33-42.5% of the Provisional Tolerable daily Intake (PTDI; 60 µg/day) (Table 2). The weekly dietary intake of Cadmium ranged between 0.02-2.97 µg/kg-bw/week (3.3 -42.5% PTWI; 7 µg/kg/bw/week).

Table 1. The mean contents of heavy metals found in crop samples from Tehran market in 2012

NO	crops Scientific names	Plant part	Lead (mg/kg DW)	Cadmium (mg/kg DW)	Chromium (mg/kg DW)	Copper (mg/kg DW)	Zinc (mg/kg DW)
1	Broccoli *Brassica oleracea var. botrytis*	leaves	7.69±0.04 n=25	1.38±0.02 n=25	0.11±0.04 n=25	33.81±0.14 n=25	64.24±0.08 n=22
2	Cabbage *Brassica oleracea Linn.*	leaves	9.30±0.03 n=25	1.56±0.03 n=25	3.51±0.11 n=25	23.11±0.11 n=25	100.06±0.09 n=22
3	Chinese cabbage *Lactuca sativa L.*	leaves	8.70±0.02 n=10	2.09±0.04 n=10	12.11±0.13 n=10	24.19±0.13 n=10	153.11±0.11 n=22
4	Spinach *Spinacia oleracea*	leaves	1.80±0.08 n=25	1.89±0.03 n=25	4.03±0.06 n=25	57.89±1.13 n=25	1069.97±0.11 n=22
5	Lettuce Romaine *Lactuca Sativa*	leaves	1.80±0.05 n=40	1.56±0.03 n=40	3.34±0.05 n=40	16.14±0.09 n=40	66.54±0.06 n=22
6	Lettuce Iceberg *Lactuca sativa L.*	leaves	1.10±0.05 n=25	1.98±0.04 n=25	3.86±0.04 n=25	15.05±0.02 n=25	41.51±0.06 n=22
7	Celery *Apium graveolens var. dulce*	petiole s	5.11±0.04 n=25	1.32±0.03 n=25	1.59±0.08 n=25	13.40±0.09 n=25	89.11±0.05 n=22
8	Cauliflower *Brassica Oleracea var botrytis*	Flower	8.90±0.01 n=12	1.36±0.03 n=12	7.72±0.09 n=12	31.04±0.12 n=12	103.21±0.05 n=22
9	Aubergine (Eggplant) *Solanum melongena L.*	Fruit	3.00±0.06 n=43	1.02±0.02 n=43	1.03±0.02 n=43	28.91±0.11 n=43	108.69±0.07 n=22
10	Onion (Red) *Allium cepa*	Bulb	1.20±0.04 n=20	1.11±0.01 n=20	4.22±0.05 n=20	11.06±0.04 n=20	168.23±0.15 n=22
11	Beetroot *Beta vulgaris*	Root	1.60±0.02 n=14	1.47±0.01 n=14	1.30±0.04 n=14	59.11±0.03 n=14	78.55±00.05 n=22
12	Potato *Solanum tuberosum*	Root	0.90±0.04 n=50	1.24±0.02 n=50	1.62±0.02 n=50	31.09±0.12 n=50	93.15±0.08 n=22
13	Carrot Daucus carota subsp. sativus	Root	3.22±0.02 n=50	1.18±0.01 n=50	5.83±0.14 n=50	19.86±0.10 n=50	179.20±0.19 n=22

Chromium is found in all vegetables. Leaves of Chinese Lettuce showed high mean content of Chromium (12.11 mg/kg DW), while Leaves of Broccoli contain low mean value of Cr (0.11 mg/kg DW). The highest daily intake of chromium in this study was 97.1µg/day, which is below the recommended dietary allowance of 130 µg/day/person (WHO 1993).

Present investigation reveals that mean concentration of Cu varies from 11.06 to 59.11 mg/kg DW. The highest mean concentration of Cu was found in Beetroot (59.11 mg/kg DW), while lowest mean concentration 11.06 mg/kg was recorded in bulbs of Onion. The Cu content of the vegetable types was below WHO maximum limit (73 mg/kg DW). Copper dietary intake studies showed differences in amounts amongst vegetable (Table 2), the estimated daily intake of Cu in this study ranged between 0.002 and 0.25 mg/day i.e. 0.07-8.3% of the Provisional Tolerable daily Intake (PTDI; 3 mg/day). The JECFA provisional maximal tolerable daily intake of Cu is 500 µg/kg bw/day and a safe upper limit of 160 µg/kg bw/day has been recommended by the Expert Group on vitamins and Minerals.

Table 2. The estimated daily intake of heavy metals by consumption of Crop samples

crops	Middle Eastern Diet: Crops Consumption (g/day)	Lead Intake (mg/day)	Cadmium Intake (mg/day)	Chromium Intake (mg/day)	Copper Intake (mg/day)	Zinc Intake (mg/day)
Broccoli (*Brassica oleraces italic*)	0.5	0.0038	0.0007	0.0001	0.0170	0.0321
Cabbage (Brassica oleracea Linn.)	5.0	0.0465	0.0078	0.0175	0.1155	0.5003
Chinese cabbage (*Lactuca sativa L.*)	0.1	0.0009	0.0002	0.0012	0.0024	0.1070
Spinach (Spinacia oleracea)	0.5	0.0009	0.0009	0.0020	0.0289	0.5350
Lettuce Romaine (*Lactuca Sativa*)	2.3	0.0041	0.0036	0.0077	0.0371	0.2374
Lettuce Iceberg (*Lactuca sativa L.)*	2.3	0.0025	0.0045	0.0089	0.0346	0.2500
Celery *(Apium graveolens)*	0.5	0.0026	0.0007	0.0008	0.0067	0.0766
Cauliflower *(Brassica Oleracea var botrytis)*	1.3	0.0116	0.0018	0.0100	0.0400	0.0865
Aubergine *(Solanum melongena L.)*	2.8	0.0084	0.0029	0.0029	0.0809	0.3043
Onion (Red) *(Allium cepa)*	23	0.0276	0.0255	0.0971	0.2544	3.8693
Beetroot (*Beta vulgaris)*	0.5	0.0008	0.0007	0.0006	0.0296	0.0393
Potato (*Solanum tuberosum*)	5.9	0.0053	0.0073	0.0096	0.1834	0.5496
Carrot *(Daucus carota subsp. Sativus)*	2.8	0.0090	0.0033	0.0163	0.0556	0.5018
PTDI[a]	-	0.214	0.06	0.06	3	60

The estimated provisional tolerable daily intake of Cu from the consumption of these ranged from 0.04 to 4.16 µg/kg bw/day, which is far below the safe daily intake limit.

The concentration of Zn was found high in Spinach (1069.97mg/kg DW); while low mean concentration of Zn was observed in leaves of Lettuce Iceberg (41.51mg/kg DW). 7 of 13 vegetable types had the mean content of Zn more than WHO maximum limit (100 mg/kg DW). As shown in Table 2, the dietary intake values for zinc ranged from about 0.03-3.87 mg/day (i.e. 0.05-6.45% of the Provisional Tolerable daily Intake (PTDI; 60 mg/day) (WHO, 1982), the EVM safe upper limit (SUL) for Zn is 42 mg/day (equivalent to 0.7 mg/kg bw/day in a 60 kg adult) for total dietary intake (Expert Group on vitamins and Mineral, Food Standard Agency, May 2003). The estimated intake of Zn from vegetable samples constituted more than 9.2% of the safe upper limit for Zn.

With increasing health consciousness and the growing number of vegetarians nowadays, vegetable safety is a very important issue. The present study has generated data on heavy metal contamination in vegetables sold in local market of Tehran city and associated risk assessment for consumer's exposure to the heavy metals. The levels of five trace metals include toxic heavy metals; lead, cadmium and chromium and two essential elements; zinc (Zn) and copper (Cu) were determined in a total of 364 vegetable samples. The concentrations of Cd, Pb, Cr and Zn in the most vegetables were greater than maximum permitted level that extended by WHO, while the Cu were present at levels below the permissible limits in food. Provisional tolerable daily intakes (PTDIs) for Pb, Cd, Cr, Cu and Zn are 0.214, 0.06, 0.06, 3 and 60 mg/day, respectively (Joint FAO/WHO Expert Committee on Food Additives, 1999). The present study showed that the contributions of these vegetables to daily intake of Pb, Cd, Cr, Cu and Zn were 21.7%, 42.5%, 161.7%, 8.3% and 6.4% of provisional tolerable daily intake (PTDI), respectively.
It can be suggested that the consumption of average amounts of these contaminated vegetables does not pose a health risk for the consumers as the values obtained are below the FAO/WHO limits for heavy metals intake.

Heavy metals have a toxic impact, but detrimental impacts become apparent only when long-term consumption of contaminated vegetables occurs. Because of the vegetables is not alone source of dietary heavy metals, certain groups of consumer such as elderly with cardiovascular problems and kidney deficiency who may intake these food items for long term should be extra cautions as they are more susceptible to toxicities.

It is therefore suggested that regular monitoring of heavy metals in vegetables and other food items should be performed in order to prevent excessive buildup of these heavy metals in the human food chain. Appropriate precautions should also be taken at the time of production, transportation and marketing of vegetables.

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