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MONITORING OF TOXIC METALS (CADMIUM, LEAD, ARSENIC AND MERCURY) IN VEGETABLES OF SINDH, PAKISTAN

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ABSTRACT
A monitoring study was carried out with the aim to assess the level of toxic metals i.e., lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg) in different vegetables grown in Sindh province of Pakistan during 2007-2008. Two hundred ten samples of twenty one vegetables were collected from farmers' field of Sindh and exporters at Karachi. These samples were grouped into four categories viz., leafy, root and tuberous, cucurbits and fruity. The samples in duplicate were digested with nitric and perchloric acid mixture with 3:1 ratio. Cadmium and Pb were analyzed with Graphite Furnace Atomic Absorption Spectrophotometer and As and Hg on Atomic Absorption using Vapor and Hydride Generation Assembly. Average concentration of Cd, Pb, As and Hg in leafy vegetables was found 0.083 μgg^{-1}, 0.05 μgg^{-1}, 0.042 μgg^{-1} and 0.008 μgg^{-1} respectively, in roots and tuberous vegetables was 0.057 μgg^{-1}, 0.03 μgg^{-1}, 0.045 μgg^{-1} & 0.004 μgg^{-1} respectively, in cucurbit vegetables was 0.021 μgg^{-1}, 0.051 μgg^{-1}, 0.056 μgg^{-1} and 0.0089 μgg^{-1} respectively and in fruity vegetables was 0.035 μgg^{-1}, 0.067 μgg^{-1}, 0.054 μgg^{-1} and 0.007 μgg^{-1} respectively. In leafy vegetables, the concentration of cadmium, lead and mercury were found comparatively higher than other three groups of vegetables. However, concentration of heavy metals found in the samples of all four categories of vegetables, was within the permissible limits and safe to consume.

Keywords: Atomic Absorption Spectroscopy, Heavy Metals, Vegetables, Graphite Furnace, Vapor Generation and Hydride Generation

INTRODUCTION
Agriculture is a complex phenomenon and exerts both favorable and unfavorable consequences on environment (Ghandi, 2000). In Pakistan, agriculture is the mainstay of national economy. The sector receives second priority after defense. Its share in GDP is about 24%. It contributes 35 % to the export earnings and employs 51 % of total labor force and play vital role in uplifting the life of 70% of rural population. Besides, major crops of Pakistan, vegetables are grown widely sufficient quantities of some vegetables such as chili, tomato etc. are exported to various countries. In Pakistan, share of vegetable export is about 0.22% (Government of Pakistan 2008-09).

Soil and environmental pollution is a matter of great concern and has been accepted as a global problem because of its adverse effect on human health, plants, animals and all exposed material to Cd, Pb, As and Hg (Irshad *et al.* 1997). Heavy metal toxicity has received special attention globally due to neurotoxin, carcinogenic and several other impacts arising from their consumption even at lower contents. (Sathawara, *et al.*, 2004). Prolonged accumulation of heavy metals through food stuff may lead to chronic effect in the kidney and liver of humans and causes disruption of numerous biochemical processes leading to cardiovascular, nervous, kidney and bone diseases (Jarup, 2003). Modern analytical techniques and ultra sensitive instruments analyzing metal contents even at ppb levels have recently resolved several health disorders associated with intake of toxic metals. Recent developments in toxicities and other disorders resulting from ingestion of toxic metals have compelled food regulators around the world to revise the safe limits of these toxicants to ensure consumer health.

Soil eco-system throughout world has been contaminated with heavy metals by various human activities and movement of metals in food chain has become human health hazard (Zahir *et al.*, 2009). Land contamination with heavy metals is increasing and becoming environmental, economic and planning issue in Pakistan (Bhutto *et al.*, 2009).

Soil chemical composition plays important role in composition of plant materials. Overall toxic metal availability in soil rhizosphere contributes to metal contents in fruits/ vegetables. Anthropogenic activity such as application of fertilizers, manures also affect soil metal content (e.g. phosphatic fertilizers being main source of Cd impurity). Soils in Pakistan contain Pb and Cd at sufficient levels (Ahmed *et al.,* 1994). Perveen *et al.* (2003) reported the presence of Cd and Pb concentration of 0.08 μgg^{-1} and 0.12 μgg^{-1} respectively toxic metals at lower concentration. Sharma *et al.* (2009) also reported Cd, Pb and As at 0.6 μgg^{-1}, 0.15 μgg^{-1} and 0.008 μgg^{-1} respectively in leafy and fruity vegetables. Leafy vegetables accumulate much higher contents of heavy metals as compare to other vegetables because leafy vegetables are most exposed to environmental pollution because of large surface area (Itanna *et al.*, 2002). Considering the significance of these metals and food consumption patterns, a detailed study was carried out to monitor levels of lead, cadmium, arsenic and mercury in different vegetables grown in the province of Sindh. The aim of this study was to monitor the toxic heavy metals Cd, Pb, As and Hg in vegetables.

MATERIALS AND METHODS

Two hundred ten (210) samples of vegetables i.e. leafy vegetables (Coriander, Methi, Spinach and Mint), root and tuberous vegetables (Arum, Onion, Potato, Radish, Sugar Beet and Turnip), cucurbit vegetables (Bitter Gourd, Cucumber, Indian Squash and Pumpkin) and fruity vegetables (Brinjal, Cabbage, Cauliflower, Chilies, French Beans, Okra and Tomato) were collected from farmers' field of Khairpur, Sukkur, Hydrabad and Karachi district and from exporters of Karachi. Samples were placed in polyethylene bags and brought to laboratory for analysis. All samples were washed with tape water followed with DDI (double de-ionized distil water). Samples were cut in into small pieces and dried at 105°C for 18 hours (Wiermans *et al*., 1986). After drying the samples were ground into powder form. Approximately 1.0 g of each sample in duplicate taken into digestion tubes, were soaked in 40ml of nitric acid and perchloric acid (3:1) and left overnight for complete contact of material. Next day, samples were digested first at 120°C for 2 hrs and then 180°C on heating digester (VELP Scientifica) till the solution becomes transparent. Digestion stopped when sample solution reduced to 2-3 ml. Cooled samples were transferred into

100 ml volumetric flask and volume raised up to the mark with 0.1 M HNO_3 (AOAC 2000). All glasswares including digestion tubes were soaked with 30% HNO_3 for 8 hours and finally washed with DDI water (Robert *et al*., 1987). Following the instruction of Instrument operational manual provided by manufacturer, analysis of Cd, Pb, As and Hg was carried out using Atomic Absorption Spectrophotometer coupled with Graphite Furnace and Vapor and Hydride generation assembly. Cadmium and Pb was analyzed on Graphite Furnace Atomic Absorption Spectrophotometer and As and Hg on Atomic Absorption using Vapor and Hydride Generation Assembly.

RESULTS AND DISCUSSION

Heavy metals are of great significance in ecochemistry and ecotoxicology because of their toxicity at low levels and tendency to accumulate in human organs (Viqar *et al* 1992). The results obtained are given in Table 2 to 4. The dietary limit in food and food stuff for cadmium is 0.1 μgg^{-1} (Table 1). High concentration of cadmium exerts detrimental effects on human health and causes severe diseases such as tubular growth, kidney damage, cancer, diarrhea and incurable vomiting. Results of the study (Table 2 to 4) show that among the four groups of vegetables, the maximum concentration (0.09 μgg^{-1}) of cadmium was found in leafy vegetables (fenugreek/ methi) whereas the minimum concentration (0.002 μgg^{-1}) was in cucurbit vegetables (Indian squash). Nergus *et al.* (2005) also reported high concentration (2.5 μgg^{-1}) in fenugreek/ methi).The concentration of lead if exceeding the maximum permissible limits (0.2 μgg^{-1}) in human, affect nervous system, bones, liver, pancreases, teeth and gum & causes blood diseases. Results of our study show that maximum concentration (0.15 μgg^{-1}) of lead was found in leafy vegetables (coriander) and the minimum concentration (0.001 μgg^{-1}) in root/ tuberous vegetables (sugar beet). Parveen *et al* (2003) also reported the similar trend of lead distribution in vegetables.

Mercury is more toxic than Cd and Pb. The concentration of mercury exceeding the maximum permissible limit (0.03 μgg^{-1}) in food and food stuff cause serious health problems such as loss of vision, hearing and metal retardation and finally death occurs. This study show that the maximum concentration (0.02 μgg^{-1}) of mercury was found in leafy vegetables (fenugreek/ methi) and the lower concentration (0.001 μgg^{-1}) was found in root/ tuberous vegetables (potato and turnip).

Arsenic is extremely toxic. The concentration of arsenic exceeding the maximum permissible limit (0.03 μgg^{-1}) in foodstuff cause short term (nausea, vomiting, diarrhea, weakness, loss of appetite, cough and headache) and long term (cardiovascular diseases, diabetes and vascular diseases) health effects. Results show that the maximum concentration (0.083 μgg^{-1}) of arsenic was found in fruity vegetables (okra) whereas the minimum concentration (0.014 μgg^{-1}) was also detected in vegetables (cauliflower).

Table 1: Permissible limits (FAO/WHO 1999) of the metals (μgg^{-1})

Permissible Limits	Cadmium	Lead	Arsenic	Mercury
	0.1	**0.2**	**0.1**	**0.03**

Table 2: Concentration (μgg^{-1}) of toxic metals in leafy vegetables

S #	Commodity	No. of samples	Average metal concentration (μgg^{-1})			
			Cd	Pb	As	Hg
1	Coriander	10	0.084 ±0.005	0.150** ±0.0055	0.031 ±0.0028	0.001* ±0.00024
2	Fenugreek/ Methi	10	0.090** ±0.0035	0.059 ±0.0036	0.065** ±0.0036	0.020** ±0.0008
3	Spinach	10	0.087 ±0.003	0.010* ±0.0011	0.016* ±0.0017	0.009 ±0.00021
4	Mint	10	0.071* ±0.003	0.012 ±0.0013	0.057 ±0.003	0.005 ±0.00022

± = Standard deviation
* = Minimum concentration
** = Maximum concentration

Table 3: Concentration (μgg^{-1}) of toxic metals in root/ tuberous vegetables

S #	Commodity	No. of samples	Average metal Concentration (μgg^{-1})			
			Cd	Pb	As	Hg
1	Arum	10	0.086** ±0.0037	0.022 ±0.002	0.017* ±0.0024	0.010** ±0.00085
2	Onion	10	0.079 ±0.0048	0.006 ±0.001	0.023 ±0.0024	0.009 ±0.00053
3	Potato	10	0.040* ±0.0031	0.091** ±0.0044	0.025 ±0.0022	0.001* ±0.00010
4	Radish	10	0.045 ±0.003	0.043 ±0.0026	0.090** ±0.0030	0.005 ±0.00022
5	Sugar beet	10	0.047 ±0.0035	0.001* ±0.0002	0.038 ±0.0027	0.005 ±0.00030
6	Turnip	10	0.050 ±0.0033	0.019 ±0.0014	0.081 ±0.0051	0.001* ±0.00016

Table 4: Concentration (μgg^{-1}) of toxic metals in cucurbit vegetables

S #	Commodity	No. of samples	Average metal Concentration (μgg^{-1})			
			Cd	Pb	As	Hg
1	Bitter gourd	10	0.016 ±0.0020	0.018* ±0.0017	0.039* ±0.0025	0.0091 ±0.0005
2	Cucumber	10	0.037** ±0.0039	0.069** ±0.005	0.042 ±0.0032	0.0056* ±0.0004
3	Indian Squash	10	0.002* ±0.00047	0.055 ±0.004	0.090** ±0.0026	0.0110** ±0.00067
4	Pumpkin/ Loki	10	0.032 ±0.0032	0.065 ±0.0067	0.053 ±0.0042	0.0100 ±0.00075

Table 5: Concentration (μgg^{-1}) of toxic metals in fruits vegetables

S #	Commodity	No. of samples	Average metal Concentration (μgg^{-1})			
			Cd	Pb	As	Hg
1	Brinjal	10	0.025 ±0.0031	0.036 ±0.0042	0.035 ±0.0039	0.007 ±0.00056
2	Cabbage	10	0.049 ±0.0061	0.084 ±0.0061	0.091** ±0.0106	0.003* ±0.00042
3	Cauliflower	10	0.075** ±0.0064	0.088 ±0.0105	0.014* ±0.0024	0.009 ±0.00103
4	Chilies	10	0.018 ±0.0034	0.041 ±0.0054	0.053 ±0.0068	0.010** ±0.00113
5	French beans	10	0.029 ±0.0037	0.089** ±0.0108	0.080 ±0.0093	0.008 ±0.00102
6	Okra	10	0.013* ±0.0024	0.064 ±0.0062	0.083 ±0.0073	0.009 ±0.00100
7	Tomato	10	0.071 ±0.0086	0.009* ±0.0017	0.025 ±0.0038	0.005 ±0.00072

CONCLUSION AND RECOMMENDATION

Present study shows that the concentration of cadmium, lead and arsenic were comparatively high in leafy vegetables. The reason for this trend is because of high translocation and transpiration rate of leafy vegetables in which transfer of metals from root to stem and ultimately to fruit is longer which results in lower accumulation other than leafy vegetables. Objective of this study was to monitor the levels of toxic heavy metals (Cd, Pb, As and Hg) in different vegetables grown in Sindh. Results revealed that the studied vegetables grown in Sindh, Pakistan, contain only the trace amount of these toxic metals. The concentrations found were within the permissible limits given by W.H.O/ F.A.O (1999) and safe in consumption point of view.

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