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Risk assessment of toxic elements in vegetables, soil and water grown in Larkana, Sindh, Pakistan

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Abstract

The purpose of this study was to evaluate risk of toxic elements in vegetables, associated soil and ground water samples collected from the surroundings of Larkana city, Sindh, Pakistan. The level of four toxic elements, such as chromium, cadmium, copper, and arsenic were determined in vegetables, soil and groundwater. The toxic elements were measured by using inductively coupled plasma optical emission spectrometer after microwave digestion system. The severity of toxic elements is evaluated through estimated daily intake, bioaccumulation factor and target hazard quotient. It was revealed that the estimated daily intake and target hazard quotient of all four examined trace and toxic elements Chromium, Cadmium, Copper, and Arsenic in vegetables samples were within the limits. Cadmium in groundwater was found 0.005mgL^{-1} which is more than Word Health Organization tolerable permissible limits. The order of Targeted hazard quotient and Estimated daily intake values of the examined toxic elements were Cd < Cr < Cu < As and As < Cd < Cr < Cu. It is revealed that the targeted hazard quotient and estimated daily intake in all vegetables samples were less than 1. It indicates that there is no serious impact of these toxic elements to the local inhabitants.

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Introduction

Vegetables are important diet of food used by human beings across the world. These are cheapest, most abundant and fresh sources of our food. About thirty five different types of vegetables are grown in Pakistan, in which tomato, round melon, lady finger, brinjal, green chili, bitter gourd and cauliflower are common (Jamel Ahmed Baig *et al.,* 2012).The most important foodstuff is mutton and chicken, yet different vegetables are being preferred and ate by many people in Pakistan for lunch and dinner. Vegetables provide fiber, minerals and vitamins, which helps to maintain the level of cholesterol in blood, and reduce cardiovascular diseases and digestion problems (Joanne L *et al.*, 2012).

Vegetables are considered as contamination free sources of food. These are being polluted due to application of pesticides to kill the insects, excess uses of fertilizers for increasing production, and non-scientific transportation methods. The industrial activities also contribute toxic heavy elements pollution in food crops due to their mixing with water (Fernando Carvalho 2006). It is a fact that increasing population requires more food, thus such situation compels the farmers to use artificial methods for increasing crop production to fulfill the needs of human beings (PB Tchuwou 2012; Vhathutshelo L, Muedi 2018). The contamination of vegetables takes place in every corner of the world (Khan *et al.,* 2008).

The cultivation of vegetables in selected area is actually depends on the canal water which comes directly from the River Indus. Sometimes, there is a shortage of fresh (canal) water coming from the river, thus the farmers use groundwater for irrigation, because river water is not available for entire days of the year (Obuobieet *et al.,* 2006). Contamination of vegetables may take place from the impure water and polluted soil to the plant (Samuel .T A. *et al.,* 2018). Soil may be contaminated through industrial effluents and wastes, and over dose of fertilizers, pesticides, herbicides and aerosol sprays (M.B *et al.*, 2003; Demireze. D *et al.*, 2006). Toxic heavy elements, chromium (Cr), cadmium (Cd), copper (Cu), and arsenic (As) may reach to the vegetables through contaminated water and soil (Powers K M *et al.*, 2003; Jarip. 2003; G. U. Chibuik *et al.,* 2014).

In earth crust , the seventh most hazardous element is chromium (Mohantry *et al.,* 2013) and it is highly toxic causes respiratory problems, lungs cancer, damage of liver, kidneys and change of genetic material in the end death (Monisha *et al.,* 2014). Cadmium is also more dangerous toxic heavy metal if elevate the recommended limts of WHO/FAO, as it bio-accumulates and has a long half-life period of about 30 years. It causes health disorders, kidney problems, lung cancer, unbalance of central nervous system, destabilize DNA, and failure of reproductive system (Givianrad *et al.*, 2009; Mohajar *et al.,* 2012; WHO, 2007). Copper is an essential trace micronutrient and it does act as a biocatalysts. It is necessary for pigmentation of body and maintains health of humans including central nervous system. (Sobukola, O. P *et al.*, 2010). The level exceeds the safe limit recommended by FAO/WHO then may lead to coma, sporadic fever and hypertension (Waleed *et al.,* 2018). Arsenic (As) is one of the abundant elements in the earth's crust. It is tasteless, colorless, and odorless Arsenic is also one of the toxic elements which are harmful for living organisms because of carcinogenic activities (Waalkes M.P *et al.,* 2003). Its contamination causes skin cancer, and damage of digestive system. It may enter into body through contaminated drinking water, vegetables and fruits (Monishajaishankar *et al.,* 2014) (Pott, W.A *et al.*, 2001).

The impact of toxic elements can be analyzed using different techniques, like estimated daily intake (EDI), bio-concentration factor (BCF) and targeted health quotients (THQs). Estimated daily intake (EDI) is a ratio between toxic heavy metal and oral reference dose that is the maximum level at which no health effects expected (Tsafe *et al.,* 2012; MdSaiful Islam *et al.,* 2014). The bio-concentration factor (BCF) of toxic elements is the transference of toxic elements from soil to plants. If calculated ranges of BCF are above than one 1.0, then it indicates higher uptake of toxic elements in vegetables than in the soil.

Since the targeted health quotients (THQs) is a human health risk assessment concerned with the accumulation of vegetables used by the residents.

Chromium, cadmium and arsenic are enormously entering in our surroundings and are the principal contaminants of many food stuffs (Jasim Uddin A, *et a.,* 2011; H. Chen *et al*., 2016). These are unnecessary elements having no major role in the growth of muscles, bones and other human health perspective (Powers K M *et al.* 2003; Jarup L. 2003). Human's health may be affected by toxic heavy metals directly as well as indirectly as these elements cannot be decomposed naturally (Wang *et al.,* 2001). The prolong use of vegetables contaminated by hazardous metals can increase their level in the tissue of human beings create acute or chronic health problems (X. Wang *et al.,* 2005). It is therefore necessary to examine the level of toxic metals cadmium, chromium, Arsenic and copper on the vegetables, groundwater and soil of the Larkana city in Sindh province Pakistan. Such study was not conducted by any researcher or organization in the past.

This study was carried out to evaluate the intake of toxic elements via fresh vegetables, maximum, average, and minimum level of target hazard quotient (THQ), and bio-concentration factor of these elements in seven famous vegetables cultivated in Larkana Sindh.

Materials and methods

Study area

Larkana is 4th populated district of Sindh province after Karachi, Hyderabad, and Sukkur. In this study, the surroundings of Larkana city of the district Larkana were selected, where the vegetables are frequently grown by the local formers. Fig. (1) show the map of study area where the samples have been taken for analysis. The sampling locations were Rehmatpur (27°36'15" North 68°13'18"East), Otha Goth (27°49' 8937" North 68°19' 6834" East), Baksho Khan Village (27°36'15"North 68°13'18"East), Bakarani (27°45' 2415"N 68°17'6875"E) and Jagirani Goth (27°68°4295" North 68°.14'7947" East). All the samples were collected following by random sampling method using global positioning system (GPS).

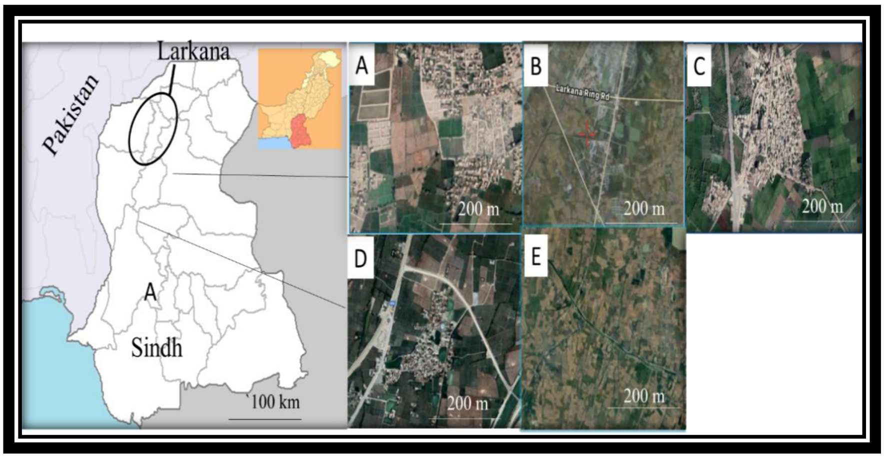

Fig. 1, Map of District Larkana with different sampling locations (A) Rehmatpur (B) Othagoth (C) Baksho khan (D) Bakrani (E) Jagirani village.

Collection of samples

A total 175 samples were collected from the selected locations of seven different vegetables, i.e. brinjals, green chilies, ladyfingers, tomatoes, round melons, bitter gourd and cauliflowers (n=25) from five sampling locations of the study area. Besides that, 25 groundwater samples from tube wells or motor pumps and the samples of soil were taken from all selected locations. The samples of soil were taken with a special instrument named auger made up of stainless steel from depth of 0-25cm. All the vegetables, water and the samples of soil were collected in spring season in the months of February through April 2018. The collected vegetables samples were kept into prewashed polyethylene plastic bags and then transported to the laboratories of Shah Abdul University Khairpur on the same day. Each collected sample of vegetables first washed carefully with the tape water and then distilled water followed by deionized water in order to remove extra contamination. The edible parts of vegetable samples already washed with deionized water were cut into small pieces with special small size of knife washed with sterilized water and put into the oven then dried at 80°C to attain the constant weight. Every dried vegetable sample was grinded using special type of machine grinder at 65-mesh sieve.

The powdered vegetable samples then preserved into a special stopper glass container (Tiwari *et al.,* 2011).

Chemical Digestion of Vegetable Samples

First, two (2.0) g of each sample of vegetable was placed into a beaker then reagent $HClO_4$ and HNO_3 was added at a ratio of 1:4. After mixing of acids, beaker containing vegetable samples were placed on electric hot plate until and unless the clear transparent solution was obtained. The complete digested samples were then filtered through Whatman 42# paper then deionized water was introduced for dilution up to 50 mL (Jasim Uddin A, *et al.,* 2011) and finally kept at a room temperature for further analysis.

Pre-treatment of soil samples

At first, took 5 g of powdered soil sample into 250ml of boro glass conical flask before washed by tape water then distilled water followed by deionized water. Then, 20ml mixture of two strong acids 0.05N HCl and 0.05N H_2SO_4 were introduced into each beaker containing soil sample.

The conical flasks containing soil samples were stirred gently for a period of 20 minutes up to dissolved residues into two strong acids hydrochloric acid and sulphuric acid. After that, each soil samples were filtered through whatman # 42 filter paper into 50ml of transparent plastic bottle for further instrumental analysis (Sahito ATG *et al.,* 2002).

Pre-treatment of water samples followed by microwave digestion method

For each sample, five hundred ml of ground water sample was introduced into a beaker, then placed two to three drops of concentrated HNO_3 and heated at 70°C on electric hot plate for drying. The residues were then dissolved in (2N. HNO_3) nitric acid followed by the addition of 33% H_2O_2 hydrogen peroxide heated at 70°C and last volume is made up to 20ml by the addition of deionized water (Greenberg *et al.,* 2012). Similarly the blank reagent was also made by adopting the same procedure.

Instrumentation

For present study, all samples were analyzed by using sophisticated instruments Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Optima 8000 Perkin Elmer (USA) was used for analysis of chromium, cadmium and copper in all samples. Arsenic was measured in Graphite furnace mode (Perkin Elmer USA). The internal calibration standard solutions containing 1.0 mg/L chromium (Cr), cadmium (Cd) and copper (Cu) were purchased from Perkin Elmer (USA). To cover extensive range of toxic heavy elements used one (1.0)mg/L as a tuning solution.

All test batches were assessed by an internal quality approach and certified if they validate the defined internal quality controls. For every test, a blank solution was run with certified reference material and then the samples were analyzed in duplicate to remove any batch specific error. Material, NIST, 1547 was used as certified reference material in every sample batch/lot to validate the precision and accuracy of the chemical digestion technique and for consequent analyses.

Analysis of Data

The data analysis was made using three indicators, namely estimated daily intake of toxic elements from vegetables, bio-concentration factor and targeted health quotients. The estimated daily intake of metals depends on the mean concentration of metals in the vegetables ingestion along with body weight. Equation

(1) was used for the estimation of daily intake of metals (MdSaiful Islam and Hoque, M. F. 2014).

$$\text{Estimated Daily Intakes of metals} = \frac{\text{Daily Intake of elements/ Metals}}{\text{Body Weight}} \quad [1]$$

The consumption of vegetables on daily basis was taken as 166g by adult, while the average weight of adult was considered as 60kg (Bangladesh Bureau of Statistics; 2010). Bio-concentration factor (BCF) is the transfer of toxic elements from the soil to eatable parts of plants, like vegetables. It is calculated as the concentration of toxic elements ratio in the vegetables to the corresponding soil from which vegetable samples were taken on the basis of dry weight using Equation (2).

$$\text{The bioconcentration factor} = \frac{[\text{M}]\text{plant}}{[\text{M}]\text{soil}} \quad [2]$$

Targeted Health Quotients (THQs) is a human health risk assessment concerned with the accumulation of vegetables used by the local residents. Targeted Health Quotients (THQs) of toxic elements has been computed using Equation (3).

$$\text{THQ} = \frac{\text{EF}\times\text{ED}\times\text{FI}\times\text{MC}}{\text{Rfd}\times\text{BW}\times\text{AT}} \times 10^{-3} \quad [3]$$

where THQ is the targeted hazard quotient, EF is the exposure frequency which is considered as one year 365 days/year, whereas 70 years considered as exposure duration 'ED', MC is considered as toxic element concentration in mg/kg, oral reference dose 'Rfd' measured in mg/kg, average body weight considered as 'BW' which is sixty kilogram, AT is considered as average time taken to non-carcinogen "365 days/ year × number of exposure years, assuming 70 years in this study" (Hang Zhou *et al.*, 2016).

The recommended oral reference dosages are 0.003mg/kg for Cr, 0.001mg/kg for Cd, 0.04mg/kg for Cu and 0.0003mg/kg for As (USEPA, 2015). If the targeted health quotient of metals are below than one then that is in safe limit, whereas THQ level is one or more than one, then threat may create to local inhabitants.

Results and discussion

The average, range and standard deviation of the observed values of toxic elements in eatable parts of various vegetables (Table 1). In vegetables samples, the concentration of elements was found different in the different types of vegetable samples. These values were arranged on the basis of toxicity, level of food contamination and health importance. The basic difference in elemental concentration in various vegetable samples inferred that each vegetable variety has its own ability to accumulate various toxic elements.

Table 1. Toxic elements contents (mg/kg fw) in vegetables from Larkana, Sindh, Pakistan.

English Name	Scientific Name		Cr	Cd	Cu	As
Brinjals, (n=25)	*Solanummelongena*	Mean ± SD	0.39 ± 0.093	0.41±0.12	2.94±0.28	0.06±0.007
		Range	0.26-0.71	0.13-0.84	2.46-3.5	0.05-0.07
Green chilies, (n=250	*Capsicumannuum*	Mean ± SD	0.408±0.141	0.36±0.16	2.33±1.18	0.094±0.042
		Range	0.34-0.57	0.14-0.64	1.61-2.76	0.06-0.12
Ladyfingers, (n=25)	*Abelmoschusesculentus*	Mean ± SD	0.428±0.13	0.48±0.04	4.42±1.46	0.082±0.016
		Range	0.33-0.56	0.14-0.65	4.3-4.66	0.04-0.15
Round-melons, (n=25)	*Cucumis melon*	Mean ± SD	0.46±0.057	0.46±0.011	1.80±0.151	0.062±0.001
		Range	0.33-0.6	0.24-0.65	1.55-2.42	0.03-0.09
Tomatoes, (n=25)	*Lycopersicanesculentum*	Mean ± SD	0.46±0.207	0.44±0.147	1.86±0.724	0.068±0.027
		Range	0.27-0.59	0.24-0.65	1.49-2.36	0.05-0.1
Bitter-gourds, (n=25)	*Momordicacharantia*	Mean ± SD	0.59±0.196	0.37±0.193	1.66±0.612	0.074±0.031
		Range	0.5-0.71	0.15-0.65	0.54-2.65	0.03-0.12
Cauliflowers, (n=25)	*Brassicaoleraceabotrytis*	Mean ± SD	0.46±0.199	0.39±0.075	1.48±0.096	0.1±0
		Range	0.28-0.70	0.24-0.55	1.35-1.58	0.09-0.11
(FAO/WHO, 2011)			0.60	0.50	5.0	0.10

Level of Toxic Elements in Examined Samples

The average and range of chromium concentration in brinjals, green chilies, ladyfingers, round melons, tomatoes, bitter gourds and cauliflower were 0.39mg/kg and 0.26-0.70mg/kg, 0.41mg/kg and 0.34-0.57mg/kg, 0.43 mg/kg with a range of 0.33-0.56mg/kg, 0.46mg/kg and 0.33-0.60mg/kg, 0.46mg/kg and 0.27-0.59mg/kg, 0.59mg/kg and 0.50-0.71mg/kg, and 0.46mg/kg and 0.28-0.7mg/kg. The level of chromium concentration in brinjals and tomatoes was detected below than the reported values of Latif *et al*. (2018) with 3.0mg/kg and of (Fawad Ali *et al.,* 2017) with 9.23-18.95mg/kg. All the above intended values of chromium in all vegetables samples were within the allowable limit of WHO and FAO; 2011 which is 2.3mg/kg.

The average and range of cadmium concentration in brinjals were 0.40mg/kg and 0.13-0.84mg/kg, in green chilies 0.36mg/kg and 0.14-0.64mg/kg, in ladyfingers 0.48mg/kg and 0.14-0.65mg/kg, in round melons 0.46mg/kg and 0.24-0.65mg/kg, in tomatoes, 0.44mg/kg and 0.24-0.65mg/kg, in bitter gourds 0.37mg/kg and 0.15-0.65mg/kg, and in cauliflower 0.39mg/kg and 0.24-0.55mg/kg.

The average concentration of cadmium in brinjals samples were nearly within same values as 0.42mg/kg reported by (Rafiqual Islam *et al.,* 2018), in ladyfingers slightly higher as compared to the work of (Odoh Rapheal *et al.,* 2011), and in round melons, the values were higher than standards of FAO/WHO, 2011. The average concentration of cadmium in tomatoes was found similar as reported by (GomaaNour-Eldein Abdel-Rahman *et al.,* 2018). Overall, the average concentration of cadmium was detected higher in almost all vegetable samples than permissible limit of 0.2mg/kg given by WHO and FAO, (2011).

The average and range of copper concentration in brinjals, green chilies , ladyfingers, round melons, tomatoes, bitter gourds and cauliflowers were 2.94mg/kg and 2.5-3.5mg/kg, 2.33mg/kg and 1.61-2.76mg/kg, 4.42 mg/kg and 4.3-4.66mg/kg, 1.80mg/kg and 1.55-2.42mg/kg, 1.86mg/kg and 1.49-2.36mg/kg, 1.66mg/kg and 0.54-2.65mg/kg, and 1.48mg/kg and 1.35-1.58mg/kg obtained. The level of copper was found within the safe limit in all examined vegetable samples proposed by WHO and FAO (2003) which is 5mg/kg.

The average concentration and range of arsenic in bringals was found 0.06mg/kg and 0.05-0.07mg/kg, in green chilies 0.094mg/kg and 0.06-0.12mg/kg, in ladyfingers 0.062mg/kg and 0.03-0.09mg/kg, and in round melons 0.062mg/kg and 0.03-0.09mg/kg.

In tomatoes the average and range of arsenic concentration was 0.068mg/kg and 0.05-0.1mg/kg, in bitter gourds 0.068mg/kg and 0.05-0.1mg/kg, and in the samples of cauliflower 0.1mg/kg and 0.09-0.11mg/kg. In general, the concentration of arsenic was also found within the allowable limits of WHO and FAO which is 0.1 mg/kg in all vegetable samples.

The average concentrations of toxic elements in all vegetable samples were found in the following decreasing order, such as Cu > Cr > Cd > As. The mean concentrations of toxic elements in different vegetables collected from the study area were compared with the standards set by WHO and FAO (2011). It was found that all samples were within safe limits except cadmium having concentration little bit higher than guidelines values.

The possible sources of elements exposure in vegetable samples of study area may be due to agricultural farms using chemical fertilizers, herbicides, chemical sprays and fungicides. Out of 25 samples of each vegetable, 32% of samples were showed slightly higher concentrations for chromium as well as cadmium as compared to the limits set by WHO and FAO (2011). In all other vegetable samples, the remaining toxic elements were within prescribed limits. Since, the percentage of contamination in all soil was found under the tolerable limits.

Estimated Influence of Toxic Elements

The mean estimated daily intake standards of chromium, cadmium, copper and arsenic are 0.004, 0.0006, 0.05 and 0.0002mg/kg fw (Table 2). It is noted that the THQ of each element via consumption of vegetables decreased in the order of cadmium < chromium < copper < arsenic.

The calculated targeted hazard quotient of each element was found less than 1.0, showing that ingestion of a single element through consumption of vegetables does not stimulate a significant potential health hazard. Total metal targeted hazard quotient value (sum of individual element targeted hazard quotient) for individual vegetable was found higher than 1 (Table 2).

Table 2. Estimated daily intake 'EDI' of trace and toxic elements (mg/kg bw) and targeted hazard quotient 'THQ'.

English Name		Cr	Cd	Cu	As	Total
Brinjals, n=25	EDI	0.0011	0.0015	0.0084	0.0013	0.0123
	THQ	0.0251	0.1743	0.0120	0.038	0.249
Ladyfingers, n=25	EDI	0.0012	0.0013	0.0012	0.0016	0.0053
	THQ	0.0277	0.1897	0.0214	0.052	0.29
Green chilies,	EDI	0.0012	0.0009	0.0064	0.0007	0.0092
n=25	THQ	0.0246	0.1394	0.0112	0.006	0.182
Round melons,	EDI	0.0013	0.0013	0.0012	0.0016	0.0054
n=25	THQ	0.0294	0.1820	0.0087	0.066	0.282
Tomatoes, n=25	EDI	0.0012	0.0012	0.0054	0.0007	0.0085
	THQ	0.0294	0.1704	0.0090	0.043	0.252
Bittergouds, n=25	EDI	0.0016	0.001 0	0.0042	0.0008	0.0076
	THQ	0.0387	0.1433	0.0080	0.0043	0.194
Cauliflowers, n=25	EDI	0.0013	0.0011	0.0056	0.0007	0.015
	THQ	0.0303	0.1549	0.0072	0.065	0.254
RfDo		0.003	0.0005	0.04	0.0003	1.4973

The order of THQ values of metals are observed as: Cd < Cr < Cu < As.

The calculated EDI values of metals in decreasing order are: As< Cd < Cr <Cu.

All calculated results for bio-concentration factors (BCF) were found less than 1.0 (Table 3). It indicates that there is high level of toxic heavy elements concentration in soil as compared to vegetables and thus, there are lower uptakes of toxic heavy elements to the vegetables (Solecki, J. *et al.,* 2002). The current results are compared with work described in literature (Table 4). In some cases, the level of toxic elements were found significantly less in different varieties of vegetables as compared to (Song *et al.,* 2009; Radwan *et al.,* 2006; Fernando *et al.,* 2012; Chary *et al.,* 2008 for Spain, Egypt, Greece, Kuwait).

Table 3. Bio-concentration factors (BCF) of trace and toxic elements.

English name	Scientific name	Cr	Cd	Cu	As
Brinjals	*Solanummelongena*	0.053	0.061	0.402	0.065
Green chilies	*Capsicumannuum*	0.056	0.049	0.319	0.038
Lady fingers	*Abelmoschusesculentus*	0.058	0.067	0.605	0.079
Round melons	*Cucumis melon*	0.063	0.061	0.246	0.038
Tomatoes	*Lycopersicanesculentum*	0.063	0.06	0.254	0.038
Bitter gourds	*Momordicacharantia*	0.082	0.05	0.228	0.039
Cauliflowers	*Brassicaoleracea botrytis*	0.064	0.05	0.204	0.038

All Vegetable indicates the BCF below < 1.0

Table 4. Concentration of toxic elements in vegetables (mg/kg) of different parts of world.

Country	Concentration of Elements				References
	Cr (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	As (mg/kg)	
Bangladesh Dhaka	1.44	0.21	18.1	0.057	MdSaiufal *et al.,* (2014)
Bangladesh Noakhali	0.64	0.058	20.6	0.05	Rehman *et al .,* (2013)
China	NA	0.19	1.18	NA	Zhuang *et al.,* (2009)
Varanasi India	NA	2.08	36.4	NA	Sharma *et al.,* (2007)
Egypt	-	0.11	4.5	-	Radwan *et al.,* (2006)
India	2.4	2.57	1.4	-	Sharma *et al,.* (2009)
Kuwait	-	0.031	-	-	Chary *et al,.* (2008)
Greece	-	0.008	-	-	Fernando *et al .,*(2012)
Spain	-	0.019	-	-	Song *et al..* (2009)
Larkana	0.484	0.376	2.02	0.086	Current study

Correlation (linear) and coefficient matrix for different elements were performed in order to explain the relations among toxic elements in vegetables. Inter elemental collaborations may illustrate the sources and pathways of the elements present in vegetables. Clear weak correlation was observed among pairs of elements in vegetable samples. Copper indicated weak correlation with other elements, cadmium showed significant positive correlation to chromium with r^2=0.55 while cadmium showed weak correlation with arsenic. These strong negative correlations among metal-metal (arsenic-copper) pair may be due to different source of elements enrichment via water and soil. The positive or nearly identical metal accumulation properties of vegetables were observed in may research findings as reported by (Abbasi *et al.,* 2013; Mohamed *et al.,* 2003; Xu *et al.,* 2013.).

Table 5. Concentration of different toxic elements in water samples of Larkana.

Sampling sites	No. samples	Cr (mgL^{-1})	Cd (mgL^{-1})	Cu (mgL^{-1})	As (mgL^{-1})
Site-01	(n=5)	0.020	0.050	0.065	0.005
Site-02	(n=5)	0.046	0.027	0.065	0.006
Site-03	(n=5)	0.026	0.039	0.102	0.004
Site-04	(n=5)	0.052	0.017	0.157	0.003
Site-05	(n=5)	0.045	0.039	0.214	0.004

Table 6. Concentration of different toxic elements in soil samples of Larkana.

Sampling sites	No. samples	Cr (mgkg)	Cd (mg/kg)	Cu (mg/kg)	As (mg/kg)
Site-01	(n=5)	0.30	0.38	1.14	0.16
Site-02	(n=5)	0.31	0.36	1.56	0.17
Site-03	(n=5)	0.40	0.25	1.55	0.11
Site-04	(n=5)	0.30	0.30	1.64	0.09
Site-05	(n=5)	0.42	0.60	1.50	0.13

The maximum concentration of chromium in groundwater was found in sampling site of 04 which was found 0.052mgL^{-1}, minimum concentration was observed 0.02mgL^{-1}. In case of cadmium, all groundwater samples were found more than allowable of WHO which 0.005mgL-1 is. The level of copper was within guideline value as proposed by FAO/WHO (2011). The concentration of Arsenic was noted up to 0.006mgL^{-1} in groundwater samples which is also within safe limits as given in Table 5. The average concentration of chromium, cadmium, copper and arsenic in soil sampling sites 01, 02, 03, 04 and 05 were found within the proposed guideline of (FAO/WHO, 2011) (Table 6).

Conclusion

It has been concluded that level of chromium, cadmium and arsenic were found high in vegetables samples while level of copper was found low in all vegetables samples as proposed by WHO/FAO. Out of 25 samples of bitter gourd 8% of samples were detected with higher Arsenic concentration while in case of cadmium 4% of samples of ladyfinger, round melon, bitter gourd and tomatoes were examined above its level as prescribed FAO/WHO.

Results of associated water samples indicate the higher level of cadmium in its samples while concentrations of other metals were examined within permissible limits. Further that estimated daily exposure of trace metals indicates the value of chromium, cadmium, copper and arsenic were below < 1 and estimated daily intake (EDI) of metals via consumption of vegetables in the study area were in the order of As < Cd<Cr <Cu.

In case of bio-concentration factors (BCF) of metals were observed below < 1.0 and decreasing order of (THQ) targeted health hazard quotient ingested via vegetables were as Cd < Cr <Cu < As. (THQ) data of all mentioned elements were below than 1, it indicates by eating mentioned vegetables there is no threat to the human health of local peoples of Larkana Sindh, Pakistan.

Recommendations

Present study suggests the regular monitoring of toxic elements in vegetables and agricultural soils of study area are necessary in future. The precautionary measures should be taken in order to prevent extreme accumulation of these toxic elements in the human food chain.

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