Assessment of heavy metals in onion and potato in imported and local variety of Pakistan and Afghanistan

Adil Ud Din[1], Mohammad A. T. Abdel-Reheem[2, 3], Hussain Ullah[4], Ijaz Ahmad[1], Amir Waseem[4], Riaz Ullah[5], Azhar Ul Haq Ali Shah[1]

[1]Department of Chemistry, Kohat University of Science & Technology, Kohat-26000, Khyber Pakhtunkhwa, Pakistan
[2]Research Center, College of Science, King Saud University Riyadh, Saudi Arabia
[3]Biochemistry Department Faculty of Agriculture Ain Shams University Egypt
[4]Department of Chemistry, Quid-i-Azam University, Islamabad, Pakistan
[5]Department of Chemistry Sarhad University of Science & Information Technology Peshawar, KPK, Pakistan
Corresponding author afridiriaz@yahoo.com

Abstract: **Objectives**: Onion and potato (*Allium cepa* and *Solanum tuberosum*) are most commonly used vegetables in Pakistan. Different samples of local variety of onion and potato were collected from Khyber Pakhtunkhwa, Pakistan and few samples imported from Afghanistan. **Methods:** Heavy metal contents of these vegetable were analysed for Cr, Pb, Cu, Co, Zn, Mn, Fe, Ni and Cd using atomic absorption spectroscopy. **Results:** The order of metal contents was found to be Fe > Zn > Mn > Cu > Cr > Pb > Cd > Ni > Co in onion (local variety), and a similar pattern Zn > Fe > Cu > Mn > Pb > Ni > Cr > Cd was also observed in onion (imported variety). **Conclusion:** Higher content of Fe Zn were found in onion from Pakistan and Afghanistan respectively. Metal levels observed in vegetables were compared with WHO and established permissible levels reported by different authors. Mean concentration of Fe, Zn, Mn, Cu, Pb, Cr, Ni, Cd and Co are 45.9, 37.63, 6.76, 5.78, 2.26, 1.623, 0.745, 0.636 and 0.0950 respectively. The study concludes that the cultivation, transportation and marketing systems of vegetables may play a significant role in elevating the contaminant levels of heavy metals which may pose a threat to the quality of the vegetables with consequences for the health of the consumers of locally produced foodstuffs. The distribution and characterization of heavy metals in vegetables was studied in detail and discussed in this paper.
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1. **Introduction**

Recent researches have shown that apart from food demand; vegetable do more as a source of important ingredients which act as an antioxidant [1]. However the contamination of vegetables with heavy metals which are natural constituents of the Earth's crust and atmosphere are of major concerned from contamination and toxicity point of view [2- 3]. Heavy metals have been of interest because of their toxicity [4]. The toxic effects of heavy metals on human health and ecosystem are well documented. Increasing evidence have shown that the toxicity of heavy metals interact with humane body through different mechanism such as oxidative stress, interference with essential metals and interaction with cellular macromolecules [4].These heavy metals cannot be degraded or destroyed and enter into human body via food, water and air [2]. The uptake of heavy metal by different species of crops differs significantly based on their genetic characteristics [5-6]. Heavy metal concentration of vegetables cannot be underestimated as these food stuffs are important components of human diet [7-9]. It may be present either as a deposit on the surface of vegetables [10], or may be taken up by the crop roots and incorporated into the edible part of plant tissues. Heavy metals deposited on the surface can often be eliminated simply by washing prior to consumption, whereas bio-accumulated metals are difficult to remove [2] and are of major concern [11]. The biological half-lives of these heavy metals are long and have potential to accumulate in different body organs and thus produce unwanted side effects [12]. It cause growth retardation [13] and changes the functions of several enzymes [14]. Some heavy metals such as Cu, Zn, Mn, Co and Mo act as micronutrients for the growth of animals and human beings when present in trace amount whereas others such as Cd, As, and Cr act as carcinogens [15-16], and Hg and Pb are associated with the development of abnormalities in children [17-19]. High amount of heavy metals (Cu, Cd and Pb) in fruits and vegetables were related to high prevalence of upper gastrointerestinal cancer [20]. High levels of heavy metals in vegetables are reported from the areas having long term uses of treated or untreated wastewater [21]. Other anthropogenic sources of heavy metals include the addition of manures, sewage sludge, fertilizers and pesticides, which may affect the uptake of heavy metals by modifying the physico-chemical properties of the soil such as pH, organic matter and bioavailability of heavy metals in the soil. It was found that increasing concentrations of heavy metals in soil increased the crop uptake [22-23]. The current study presents data on heavy metals (Cu, Zn, Cd, Pb, Mn, Co, Cr and Ni) concentrations in some Pakistani and Afghani vegetables such as Onion (*Allium cepa* Family: Alliaceae) and Potato (*Solanum tuberosum*. Family: Solanaceae) grown locally in Pakistan and imported from Afghanistan and sold in open markets of District Koaht. It may be assumed that atmospheric deposition increases the level of heavy metals during transport and marketing, leading to significant contamination of vegetables at the market sites than absorption from the soil via water at the production sites. Observed concentrations of Cu, Zn, Cd and Pb in the vegetables were also compared with Prevention of Food adulteration (PFA) act [24] and European Union (EU) standards of food contamination. The study indirectly shows the heavy metals contents of the soil of the areas where these vegetables grows. The current study has also to address many health concerns which are due to the exposure of these heavy metals. This study is very important because most of the population of Pakistan depends on vegetables in their diets without the awareness that different types of vegetables absorb and/or adsorb heavy metals differently. Awareness about heavy metal contamination in each vegetable may possibly help the Pakistani to minimize or hopefully avoid such exposure. Since in our region (Kohat) it is very difficult to determine the exact source and origin of the vegetables.

2. Materials and Methods

2.1. Sample collection and pre-treatment

The study was conducted at Department of Chemistry, Kohat University of Science and Technology Kohat, during September 2011 to February 2012. Two vegetables (i.e. *Allium cepa* and *Solanum tuberosum*) commonly cultivated in different regions of Pakistan and Afghanistan were selected. Samples were washed with distilled water and then kept in pre-distilled water rinsed polyethylene bags and pined of avoid atmospheric deposition of heavy metals. Then the samples were brought to the laboratory, chopped into small pieces and dried in oven at 105^{o}C till the constant weight was obtained. To assess the concentration of heavy metals, the dried samples were powder with a stainless steel blender and passed through a 2 mm size sieve. The samples were kept at room temperature for further analysis.

2.2. Analytical procedure for heavy metal analysis

Samples of 2 gm each of *Allium cepa* and *Solanum tuberosum* were taken in a china dish from the pre-dried samples. Then the moister free sample after charring was placed in furnace. The furnace temperature was gradually increased from room temperature to 550^{o}C. The sample was ashed for about 5 hr until a grey or white ash residue was obtained. The contents of china dish were cooled to room temperature in desiccators and 5 mL of 6 M HNO_3 solution was added into China dish and when necessary, the mixture was heated to dissolve its content. The solution was filtered through whatman (#42) filter paper into 25 mL flask and was diluted to the mark. The solutions were then stored in clean and dry plastic bottles [25-26]. Determination of heavy metals such as Cr, Pb, Cu, Co, Zn, Mn, Fe, Ni, Cd in vegetable was achieved by flam atomic absorption spectrophotometer (AAS PerkinElmer Model AAnalyst 400). The instrument was calibrated using manually prepared standards solution of desire ppm for each heavy metals form the certified standard stock solution (1000 PPM-manufactured under ISO 9001 Quality Assurance system-Perkin Elmer) in the range from 0.6-9.6 ppm. Acetylene gas was used as the fuel and air as the support.

2.3. Quality assurance

Blank solution of 25 mL was prepared by adding 5 mL 6 M HNO_3 and 20 mL distilled water and quality control standards were measured at every ten samples to detect contamination and drift. The elemental concentrations of procedural blanks were generally below detection limit for all the metals. Precision and accuracy of analyses were also made sure through replicate analyses of samples. Metal contents were expressed as parts per million wet weight.

2.4. Statistical analyses

Total 6 samples; 3 each of onion and potato were analysed for metals estimation. Results of each sample were reported. Value in the text is shown in tabulated form as mean ± SD using statistical package, version 9.0 with ND as not detected.

3. Results

The mean concentration values of heavy metals in all samples are summarized in Table 2. The data presented (Table 2) showed a significant difference from the data reported in the literature (Table 1).

4. Discussion

Heavy metal exposure from vegetables has largely been ignored in day today life. This study is to focus on Pb, Cd, Cu, Co Fe, Cr, Ni and Zn concentrations in vegetables. Table 2 indicates the different classes of samples analyzed and the mean concentration range from minimum to maximum of the heavy metals in the investigated samples. Data are also summarized in Fig. 1-2. All the vegetable in this study were found to contain substantial concentration of lead, cadmium, copper, cobalt, iron, chromium, nickel and zinc. Result shows a wide range of concentration of these elements within each class. The mean values of the heavy metals vary from class to class. Exposure of chromium may be due to air breathing, drinking water and eating some vegetables containing chromium [2]. The levels of chromium were ranged from (0.67 to 3.2) mg/Kg. The highest amount was found in potato (potato-1) and the lowest in oni0n (onion-1). The abundance of chromium in these vegetables is in the order, potato-1 > potato x-tress-2 > onion-3 > potato container-3 > onion-2 > onion-1. The study showed that the maximum concentration (3.20 ± 0.01) mg/Kg of chromium in potato-1. Its bearable amount (up to 0.2 mg/day) plays a vital role in the metabolism of carbohydrates and lipid. However concentration greater than normal limit leads to toxicity and its accumulation can result in hepatitis. Maximum concentration of lead (6.83 ± 0.03) mg/Kg was estimated in onion (onion-1) and minimum concentration in potato (potato container-3) (ND). The concentration of lead was found lower than the permissible limit of (0.002 – 0.0025) mg/Kg dry weigh of lead in vegetables for human consumption. However the maximum allowable levels of lead are reported in the literature as follows: 0.006 mg/day for individuals less than 6 years, 0.015 mg/day for greater than 7 years, 0.025 mg/day for pregnant women, and 0.075 mg/day for other adults set by the USFDA in 1993 [27]. Another study reported a maximum allowable level of 0.01 mg of Pb/kg based on fresh weight [2]. The order of content of lead in vegetable was observed in the order as onion-1 > potato x-tress-2 > onion-2 > onion-3 > potato container-3. High concentration of Cu (11.0 ± 0.00) mg/Kg was observed in potato (potato xtress) while the lowest concentration was detected in onion (onion-2) (2.1700) mg/Kg. The abundance of Cu under the present study is in the order potato x-tress-2 > onion-1 > potato-1 > potato container-3 > onion-3 > onion-2. The acceptable limit for human consumption of Copper (Cu) is 10 mg/Kg [28]. When Cu exceeds its safe level concentration, it causes hypertension, sporadic fever, uremia, coma etc. The concentration of Co in the entire samples under study ranged from (ND-0.4) mg/Kg. The order of concentration of Co in the vegetable was determined as onion-1 > potato-1 > onion-2, and below detection limit in onion-3, potato xtress and potato container Deficiency of Co in diet results into pernicious anemia, severe fatigue, shortness of breath and hypothyroidism, while overdose may lead to angina, asthma, cardiomyopathy, polycythemia and dermatitis. The safety limit for human consumption of Co is 0.05 to 1 mg/day in humans [29-30]. Thus the recorded range of Cobalt concentration in vegetables falls above the safety limit during present investigation. The mean minimum and maximum concentration of Zn was found in the range from (23.7 to 52.90) mg/Kg, with lowest value found in potato container-3 and highest value in potato x-tress. The concentration of Zn in the increasing order is potato x-tress >onion-1 > onion-2 > potato-1> onion-3 > potato container-3. The concentration of heavy metals in vegetables is higher than the prescribe limit of 0.05-0.06 mg/Kg [30]. The mean levels of Mn were ranged from 4.57 to 9.85 mg/Kg. The abundance of Mn in the vegetable in the increasing order is onion-3 > onion-2 > onion-1 > potato-3 > potato-1 > potato-2. The study showed that the maximum concentration (9.85 ± 0.00) mg/Kg of Mn in vegetable under study is higher than the permissible limit of 6.61 [31]. Iron is an essential element in production of Red Blood Cells (RBCs).The Fe contents rages from (38.0-58.40) mg/Kg. High concentration (59.40) mg/Kg was found in onion (onion-3) where as low concentration value of 38.10 mg/Kg was found in potato-2. Low intake of Fe may lead to anemia, tiredness and pallid physique, while high intake may results into hepatic megaly, cardiac infraction and nephric malfunction. The acceptable limit for human consumption of iron is 8 to 11 mg/day for infants as well as adults [32]. During present investigation, the value of Fe was found much higher, which is significant due to iron rich soil of the area. In the increasing order the concentration of Mn is onion-3 > onion-2 > onion-1 > potato-3 > potato-1 >potato-2. Nickel is found in soyabeen, nuts, grain and vegetables. Onion (onion-1) showed high content of Nickle (1.30) mg/Kg while Potato-1 contain low value of Nickle (0.38) mg/Kg. the presence of Nickle rages from 0.125 to 4.493 mg/Kg in various vegetable. The increasing order of Nickle in various vegetables is onion-1 > potato-3 > onion-2 > onion-3 > potato-2 > potato-1. Deficiency of Nickel have been linked with hyperglycemia, depression, sinus congestion, fatigue, reproductive failures and growth problems in humans, while excess intake leads to hypoglycemia, asthma, nausea, headache, and epidemiological symptoms like cancer of nasal cavity and lungs. The prescribed safety limit of Nickel is 3 to 7 mg/day in humans [29]. Thus it falls within the safety limit in vegetables and can be consumed without any risk. Based on plant species, their physical and chemical properties, plants can readily absorb cadmium from soil which upon ingestion will enter into the human food chain. In the present investigation, the value of cadmium (Cd) ranges from (0.450-0.770) mg/Kg in various vegetables. The maximum concentration (0.770) mg/Kg of Cd was recorded in potato (potato-2), while minimum concentration (0.450) mg/Kg was registered in onion (onion-2). Acute doses (10-30) mg/Kg/day) of Cd can cause severe gastrointestinal irritation, vomiting, diarrhea, and excessive salvation, and doses of 25 mg of Cd/Kg body weight can cause death. Low level chronic exposure to Cd can cause adverse health effects including gastrointestinal, hematological, musculoskeletal, renal, neurological and reproductive effects [29]. Intake of Cd can double if one smokes cigrates because each cigrate contains about 2 mg Cd. The concentration of Cd in various vegetable is in the increasing order is potato-2 > onion-3 > onion-2 >potato-1 > potato-3 >onion-2. Prolong use of these metals may cause health hazard effects. Several investigations have shown that kidney damage and/ or bone effects are likely to occur at lower kidney cadmium level [33]. It was also investigated that low concentration of Cd has the same effects as high concentration [34]. This study reveals that vegetables are potential sources of heavy metals. The higher concentration of heavy metals in these vegetables may prove lethal for human beings, however, the minimum value of these obtained in this research could not be neglected. Balance concentration of heavy metals is necessary for human needs. The present investigation showed that the use of vegetables can expose user to high levels of heavy metals. Ideal exposure assessments involve three phases: source of pollutant, concentration of pollutants and doses of pollutants. The present study has only demonstrated that vegetables are notable sources of Pb, Cd, Cu, Co, Fe, Cr, Ni and Zn in human body as well as in the environment. Further study is required on the absorbed level and the number of persons exposed should be investigated for different groups of the general population in particular susceptible group and highly exposed group. In other words health implication of these metals can only be properly assessed by monitoring the level of these toxic metals in the blood and urine sample of the group engaged in the practice.

5. Conclusion

This study investigates the level of heavy metals in vegetables of different countries marketed in District Kohat, Khyber Pakhtunkhwa, Pakistan. It can be concluded from the result that some vegetables contain high concentration of heavy metals then the prescribe limit. The accumulation of heavy metals in the underground vegetables indicated the highly level of toxic metal which enters into our food chain. Although underground vegetables are the good source of Zn, Cu, Fe necessary for our good health, but by the accumulation of toxic metals like Pb, Cr and Cd, the essential micronutrients would be deficient in our diet. There is also need for further studies to ascertain the selectivity of such vegetables which are resistant to the uptake of high concentration of toxic metals and to evaluate the potential risk to human from the use of these products. The high level of heavy metals may be correlated with earth crust, waste water and transportation. It was infer from the result that most of the vegetables sold in Pakistani have been found highly contaminated with heavy metals. This research work can help in awareness of the detrimental effects caused by heavy metals.

Conflict of interest statement

We declare that we have no conflict of interest.

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Table 1; Comparision of heavy in vegetable published from different parts of Pakistan and current study (mean mg kg^{-1})

Name	Cr	Pb	Cu	Co	Zn	Mn	Fe	Ni	Cd	Methodology	Reference
Onion/*Allium cepa*	2.44	12.4						49.9	11.16	Atomic Absorption Spectrophotometer	[35]
	BDL	BDL	-----	-----	------	-----	1.405	1.075	BDL		
Potato/*Solanum tuberosum*	0.240		------	------	0.710	0.170	-----	------	0.002	Atomic absorption spectrophotometer	[36]
	0.030	BDL	------	------	-------	-------	1.800	1.655	0.045	Atomic absorption spectrophotometer	[37]
Onion/ *Allium cepa*	1.1300	3.0433	4.8100	0.4000	37.600	8.2433	47.467	0.8933	0.6133	Atomic absorption spectrophotometer	Current study
Potato/ *Solanum tuberosum*	2.1167	2.2300	6.7573	0.1700	37.667	5.2767	44.333	0.5967	0.6600	Atomic absorption spectrophotometer	Current study

BDL = Below Detection Limit

Table 2 Statistical summary of heavy metals concentration (mg/kg) in different vegetables.

Market site	Production site	Name	Cr	Pb	Cu	Co	Zn	Mn	Fe	Ni	Cd
District Kohat	Afghanistan (Kabul)	Onion-1	0.8 ± 0.02	6.83 ± 0.03	9.51 ± 0.07	0.4 ± 0.01	45.4 ± 0.02	7.22 ± 0.00	44.9± 0.04	1.31 ± 0.007	0.67 ± 0.01
	Pakistan (Mohmond Agency)	Onion-2	0.67 ± 0.01	1.48 ± 0.01	2.17 ± 0.04	ND	39.0 ± 0.00	7.66 ± 0.00	38.1 ± 0.00	0.7 ± 0.002	0.45 ± 0.00
	Pakistan (Quetta)	Onion-3	1.92 ± 0.02	0.82 ± 0.01	2.75 ± 0.00	ND	28.4 ± 0.00	9.85 ± 0.00	59.4 ± 0.01	0.67 ± 0.002	0.72 ± 0.00
Mean			1.1300	3.0433	4.8100	0.4000	37.600	8.2433	47.467	0.8933	0.6133
Minimum			0.6700	0.8200	2.1700	0.4000	28.400	7.2200	38.100	0.6700	0.4500
Maximum n = 3			1.9200	6.8300	9.5100	0.4000	45.400	9.8500	59.400	1.3100	0.7200
	Pakistan (Machanee	Potato-1	3.2 ± 0.01	ND	5.312 ± 0.01	0.17± 0.00	36.4 ± 0.01	5.45 ± 0.001	52.0 ± 0.00	0.38 ± 0.002	0.61 ± 0.00
	Pakistan (Arif Wala)	Potato x-tress-2	2.0 ± 0.01	3.88 ± 0.02	11.0 ± 0.00	ND	52.9 ± 0.03	4.57 ± 0.00	40.1 ± 0.01	0.45 ± 0.003	0.77 ± 0.00
	Pakistan (Okara)	Potato Container-3	1.15 ± 0.00	0.58 ± 0.04	3.96 ± 0.00	ND	23.7 ± 0.00	5.81 ± 0.00	40.9 ± 0.00	0.96 ± 0.002	0.60 ± 0.00
Mean			2.1167	2.2300	6.7573	0.1700	37.667	5.2767	44.333	0.5967	0.6600
Minimum			1.1500	0.5800	3.9600	0.1700	23.700	4.5700	40.100	0.3800	0.6000
Maximum n = 3			3.2000	3.8800	11.000	0.1700	52.900	5.8100	52.000	0.9600	0.7700
Over all Mean			1.6233	2.2650	5.7837	0.0950	37.633	6.7600	45.900	0.7450	0.6367
Over all Minimum			0.6700	0.0000	2.1700	0.0000	23.700	4.5700	38.100	0.3800	0.4500
Over all Maximum Total n = 6			3.2000	6.8300	11.000	0.4000	52.900	9.8500	59.400	1.3100	0.7700

ND, not detected; data are mean ± standard deviation

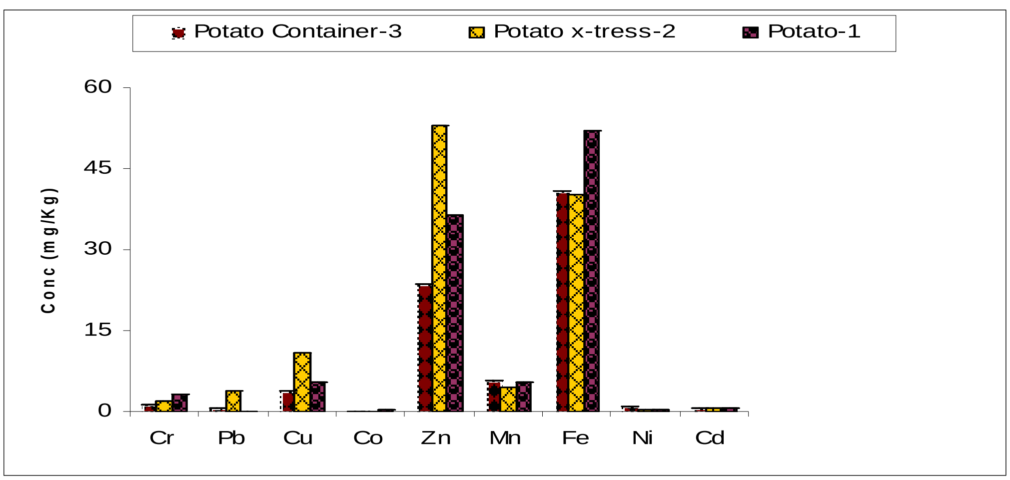

Fig 1. Bar chart represent mean concentration of heavy metals contents potatoes marketed in district Kohat, Pakistan with standard deviation as error bar

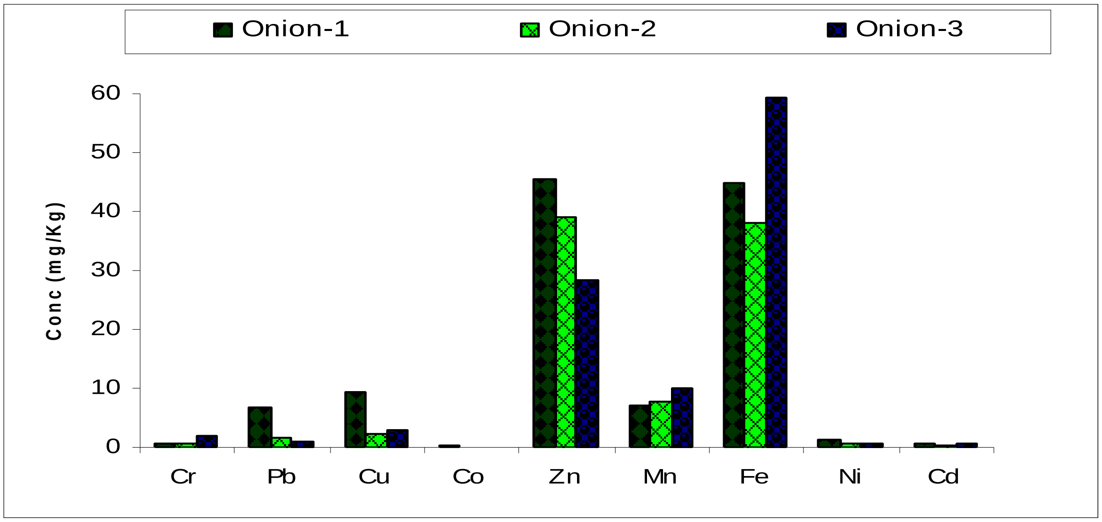

Fig 2. Bar chart represents mean concentration of heavy metals contents onions marketed in district Kohat, Pakistan with standard deviation as error bar

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