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Detection of Heavy metals in Fruits and Vegetables available in the Market of Quetta city

Khair Un Nisa*[,1,2], Samiullah[1], Naqeebullah Khan[1], Attiq-ur-Rehman[1]

[1]Department of Chemistry, University of Balochistan, Quetta 87300-Pakistan
[2]Colleges, Higher and Technical Education Department, Balochistan, Quetta 87300-Pakistan

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Abstract

This study is conducted for the determination of heavy metals concentration like Fe, Ni, Mn, Co, Cd, Cu and Pb in five edible vegetables (Cauliflower, Cabbage, Cucumber, Lady finger and Tomato), five edible Fruits (Water melon, peach, Banana, Mango (Sindhri & Langra) and apple) and peel of all these Fruits and endocarp of apple. Samples were purchased from the Local Market of Quetta city (Capital of Balochistan). Atomic Absorption Spectrophotometer ((FAAS, Thermo - Electron Corporation, S4 AA System, Ser. No, GE711544, China) double beam and deuterium background hollow cathode lamps of Fe, Pb, Cd, Co, Cu, Ni and Mn were used at specific wavelengths for the determination of heavy metals concentration. Samples were run three times and at least three or four standards are used for each metal analysis. Concentration of Fe, Mn, and copper were very much below the permissible limits defined by WHO/FAO. Concentration of Ni was found at toxic level in cucumber. Concentration of Cd was above the safe value in all samples except banana fruit given by WHO/FAO. Concentration of Co was found above the limit defined by ASTDR 1994 in all the samples. Concentration of Pb with respect to the (China food hygiene standards 1994) 0.2mg/kg and WHO/FAO 0.3mg/kg is above the limit in all samples but it found very high in Tomato, Cabbage, Cucumber, Peach and Watermelon. The overall result of this study reveals that the samples of vegetable and fruits are highly contaminated with heavy metals Co, Pb, Ni and Cd due to the usage of drainage water for watering them and their consumption can cause hazardous effect on human health.

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* Corresponding author: naqeebhmd2@gmail.com

1. Introduction

Heavy metals determination in Fruits and vegetables are an important task for nutritionists, environmentalists and scientists. Heavy metal contamination in Fruits and vegetables cannot be neglected as these foodstuffs are important components of human diet. These are rich sources of vitamins, Fiber, minerals and also have importance as anti-oxidative effects for proper growth, body development, and maintenance of overall health [1]. Other than water and soil, foods are also contaminated with heavy metals due to the use of chemicals sprays, preservatives, industrialization, mining activities, fertilizers and use of waste water [2]. Contamination of Heavy metal in fruits and vegetables is one of the most significant aspects of food quality. The pollution of heavy metals belong to the environmental pollution that occurred from man industrialization and agricultural activity in last few years [3] Environmentalists are concerned with the existence of heavy metals in the environment and to analyze

their biological effects on human health, food is the major source of heavy metals which directly upset the human health. Several studies have been carried out for the purpose of the appropriate level of undesirable metals contamination in food with and its suitability for human health [4]. There are three groups of heavy metals, Major elements (vital elements), Trace elements (heavy metals) and Ultra heavy elements. Major elements are Calcium, Potassium Sodium,, Magnesium, Chlorine, Sulfur and Phosphorus are required 50g per day, Trace elements Iron, copper Iodine ,Zinc, Manganese, Selenium, Chromium, Nickel ,Cobalt, are needed less than 50g per day while Ultra trace elements are Lead, Aluminum, Bromine, Arsenic, Barium, Mercury, Bismuth, Cadmium, Selenium Germanium, Silicon, Lithium, Rubidium, Sb, Sm, Sr, Ti, Tl, and Tungsten are not essential [5]. Processed foods, Fresh fruits, herbs and vegetables are the main sources of vital elements compulsory for proper body growth and health development in our diet. However, products of food can be polluted by toxic metals (HMs) from industrialization of food processing and other environmental activities. The toxic health effects of these contaminations are due to the deficiency of vital elements and toxicity of Heavy Metals in humans diet which require a necessary monitoring of the essential (vital elements), trace elements (Heavy metals) concentrations in the humans diet for the safety of public health [6]. Mostly non-biodegradable contaminations are metals with long biological half-lives having great possibility to gather in various body organs which leads to severe effects on human health [7]. The high concentration of Lead, Copper, Cobalt and Cadmium in our diet such as in vegetables and fruits cause the renal failure, affects the reproductive systems, cause the upper intestinal cancer, bone cancer; it also a cause of hypertension. The minute exposure to these heavy metals for long time has harmful effects on living organisms. Studies of toxicity confirm that these metals can damage the neurological function of human brain by inducing the neurotransmitter production and by transforming the large number of metabolic activities in the body [8]. The most toxic elements for human are Pb and Cd [9]. In the recorded history, today Human beings are facing the highest levels of health problems because of these metals. This is due to industrialization, coal burning petroleum, worldwide burning of unwanted waste materials and natural gas [10]. Allowable limits of some Heavy Metals or Safety values for vegetables and fruits of Pb, Cu, and Cd in suggested by the WHO/FAO are 0.3, 40, and 0.2 mg per kg [11]. Many countries in the world has developed a Regulatory frameworks and guidelines for heavy metals determination in the food stuff and environment such as Australia and New Zealand [12]. Industrial wastes and sewage water is a great problem for the modern world. Mostly it is exhausted in the agricultural lands which is used for harvesting various edible vegetables and crops. These drainage wastes are the rich source of organic matter, nutrients and carry toxic metals as Iron, Chromium, Nickel, and cobalt, Manganese, Copper, Zinc, Lead and Cadmium in the agricultural land. Vegetables uptake the heavy metals from the polluted air, soil and water which leads to elevation of contaminations level in food stuff [13]. Contaminant or heavy metal compounds are taken up by the plants together with the necessary nutrients and are transferred to the different tissues of plants organs and food chain [14]. Consumption of fruits and vegetables containing heavy metals is a main route of food chain for human exposure [15]. Heavy metals are absorbed by the different parts of plants which are exposed to the airborne deposits and also absorbed from the polluted soil and environments contaminated with heavy metal through roots. In addition to this, the irrigation of fruits and vegetables by sewage and industrial waste water also contaminate the vegetables with heavy metals [16].

2. MATERIAL AND METHOD

Study Area: The study was conducted at the Department of Chemistry, University of Balochistan Quetta, Pakistan during the months of June and July, 2019. The Fruits and vegetables are brought to the local market of city from different part of province (Kuchlak, Noshki, Khuzdar and from the vicinity of Quetta city) from other parts of country (Punjab, Sindh and Sawat) and also

imported from the neighbour countries (Afghanistan and Turkey).

Sampling: The sample of fruits and vegetable were collected from local market of Quetta city and brought to the laboratory of chemistry department, University of Balochistan, Quetta, Pakistan for the samples preparations. The common names, scientific names of vegetables and fruits and their belonging areas are given in table 1 below.

Table 1: Sample of fruits and vegetables

Common Name	Scientific Name	Areas from which they are brought to Quetta city
Tomato	Solanum lycoperiscum	Khuzdar District
Cauliflower	Brassica Oleracea Botrytis	Quetta city
Cabbage	Brassica Oleracea	Kuchlak (Khani)
Cucumber	Cucumis Sativus	Afghanistan(City Pra)
Lady finger (Okra)	Abelmoschus Esculentus	District Khuzdar
Fruits		
Mango (Langra, Sindhri)	Mangifera indica	Sindh and Punjab
Apple (Tor kulu golden)	Malus Domestica	Turkey
Peach	Prunus Persica	Sawat
Water melon	Citrullus Lanatus thumb.	District Noshki
Banana	Musa Acumiata	Karachi

Washing and drying: The fruits and vegetables collected were rinsed with distilled water properly to remove the contaminated particles. After that these were chopped to make nearly uniform small pieces. Then, these small pieces of fruits and vegetables were placed in the acid washed clean and labelled proclaim crucibles. Later, the small pieces of fruits and vegetables were dried in oven at 50°C for several hours until they become stiff and crispy.

Grinding/ sample size reduction: The dried Vegetables and fruits pieces were crushed and grounded by using mortar and piston to fine powder to get homogenized samples. Later, the dried powdered samples were stored in polyethylene bags for further process.

Digestion: 1g of accurately weighed dry ground samples was taken into the Pyrex beaker of about 100ml then strong acids (oxidizing agents) conc. nitric acid, per chloric acid and sulphuric acid with ratio of 5:1:1 about 10ml were added to it and stirred with magnetic stirrer on hot plate at 80 C^0 for 1 hour until the clear solution was obtained. Then, it was cooled and filtered into 50 ml flask through whahtman filter paper no 42, and were diluted with de-ionized water up to the mark of 50ml labelled the flask and kept for further analysis.

Analysis: The samples were analysed with help of Atomic Absorption Spectrophotometer ((FAAS, Thermo - Electron Corporation, S4 AA System, S. No, GE711544, China) double beam and deuterium background hollow cathode lamps of Fe, Pb, Cd, Co, Cu, Ni and Mn were used at specific wavelengths.

3. RESULT AND DISCUSSION

The analytical results of the present study indicate the presence of all the selected heavy metals in the studied samples of Fruits, the peels of fruits and vegetables. The results obtained for Fe, Pb, Co, Mn, Cd, Cu, and Ni vegetables, fruits and the peel of fruits are shown in table 2, table 3 and table 4 respectively while the table 5 shows the standard values. The comparison among the vegetables, fruits and the peel of fruits concentrations and with standard values are shown in figures 1 – 14.

Table 2: Heavy metals Concentration in vegetables (ppm).

Vegetables	Fe	Pb	Co	Mn	Cd	Cu	Ni
Cauliflower	3.4880	0.1158	0.3732	0.5898	0.0990	0.3687	0.2777
Cabbage	3.8874	0.7732	0.3661	0.7989	0.1085	0.3173	0.3525
Lady finger(Okra)	3.5721	0.1207	0.3856	0.5148	0.1015	0.4536	0.2115
Tomato	4.7930	0.4455	0.3385	0.5602	0.1034	0.3933	0.208
Cucumber	5.3860	0.2278	0.3841	0.7428	0.1018	0.3883	5.8191

Table 3: Heavy metal concentration in Fruits (ppm).

Fruits	Fe	Pb	Co	Mn	Cd	Cu	Ni
Water melon	3.1274	0.6777	0.3532	0.4720	0.1015	0.3059	0.1933
Peach	4.7436	0.8242	0.3699	0.5754	0.1061	0.3936	0.2046
Banana	10.1227	0.2067	0.3749	1.0426	0.0857	0.5377	0.1208
Mango (Sindhri)	5.6186	0.2322	0.3910	0.6422	0.1012	0.5466	0.2621
Mango (Langra)	5.5551	0.2758	0.4308	0.6513	0.1178	0.5680	0.1128
Apple	4.2133	0.2321	0.4049	0.5145	0.1140	0.4535	0.1533
Endo carp of apple	7.2568	0.0511	0.4571	0.6331	0.1161	0.5419	0.1785

Table 4: Heavy metals concentration in Peels of fruits (ppm).

Peel of fruits	Fe	Pb	Co	Mn	Cd	Cu	Ni
Water melon	3.0889	0.2745	0.4376	0.6385	0.1245	0.5739	0.1609
Peach	10.7672	0.1354	0.3908	0.8833	0.1045	0.5556	0.1585
Banana	5.9038	0.1814	0.3923	1.1091	0.1025	0.4500	0.1389
Mango	4.3927	0.2364	0.4174	0.5556	0.1120	0.4938	0.1070
Apple	6.6414	0.0154	0.4427	0.8508	0.1121	0.4372	0.2104

Iron: It is an essential trace metal. A very small amount of Fe is required for cellular functions of body; Iron is a major constituent of haemoglobin in red blood cells which transport oxygen to the body cells. Men and Women of all the age groups require Fe at various amount, Post-menopausal women and men require 8mg/day, Women with Pre-menopausal stage Require 18mg/day, Pregnant Women Require 127mg/day and a child about six require 11mg/day. The deficiency of Fe cause Anima shortness of breath at night and spoon shaped nails, its high dose decrease the absorption of Zn and cause liver cancer and heart disease [17].The concentration of iron in fruit samples such as banana and Endo carp of apple were detected greater than all the vegetable samples while rest of the fruit samples showed no any difference. In addition, the concentration of iron in the peels of peach and apples were determined greater than vegetable samples. However, there was no any important difference in the quantity of iron between the fruits and the peels of fruits samples. The concentration of iron in all Fruits and vegetable samples is much below the permissible limit (425 ppm) as shown in figures 1 & 2 respectively.

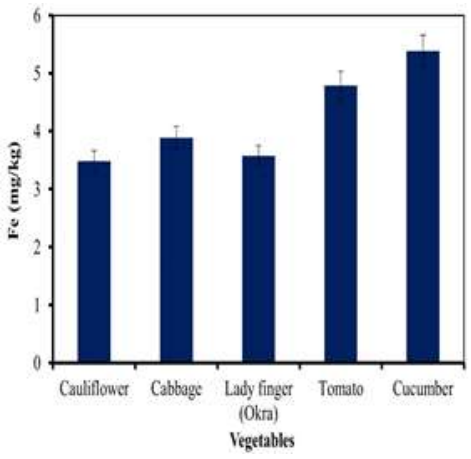

Figure 1: Concentration of iron in vegetables

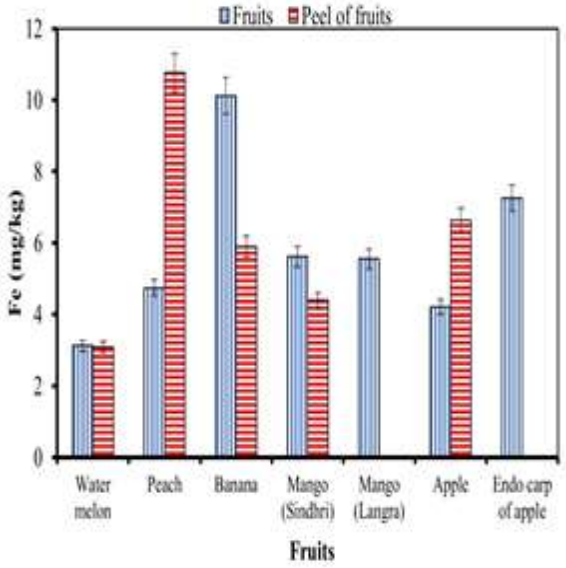

Figure 2: Concentration of iron in fruits & peels of fruits samples

Lead: It is not essential heavy metal and is highly toxic for microorganisms, plants and animals, its use in very small quantity can cause environmental and health problems that affect the multiple body systems, Pb can enter the body through breathing in air contaminated with Pb as it gets into the lungs transported into the other parts of the body and is deposited into the bones. It affects the central nervous system, I.Q of children and behaviour, Alteration in sperms decrease the fertility in men and increase the chance of miscarriage and defects in birth in women [18].

The concentration of lead in the fruit samples such as peach was observed higher than all the vegetable samples whereas other fruit samples showed no any important difference. The fruit samples such as water melon and peach indicated higher concentration of lead than the peels of all fruit samples The concentration of Pb crossed the safe values in all samples of fruits and vegetables except lady finger and cauliflower in which concentration of Pb lies in safe limits. Permissible limit for Pb was 0.3 ppm set by WHO/FAO (Figures 3 & 4).

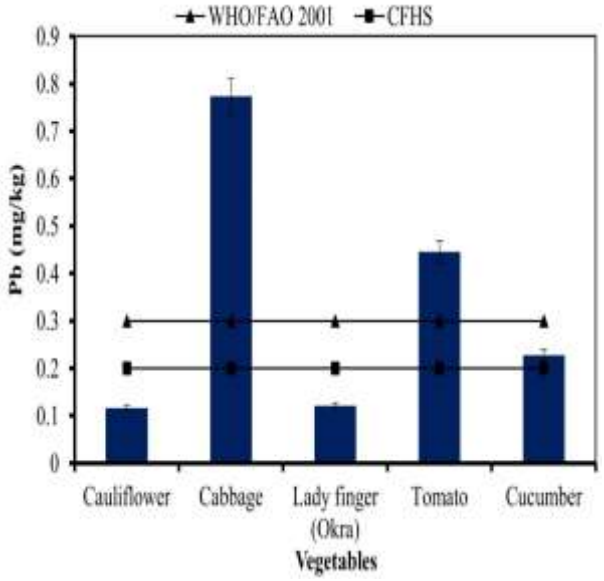

Figure 3: Concentration of Lead in vegetables sample

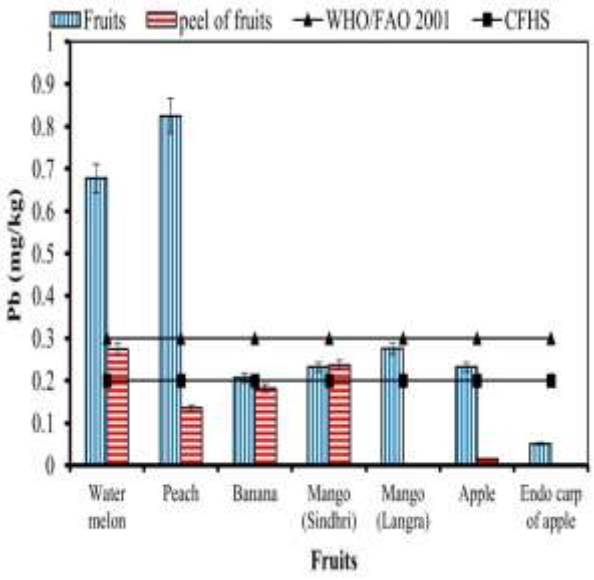

Figure 4: Concentration of lead in fruits & peels of fruits samples

Cobalt: Cobalt is naturaaly occouring element. It is very important component of Vitamine B12 which helps in producing red blood cells, Co jobs like Zn and Mn.therefore it can replace Zn in some biochemical reactions. The deficiency of Co cause anemia.The intake of Co greater than 30mg/day cause toxicity which can affect the heart muscles, congestive heart failure, digestive & skin disorder in human [11]. The concentartion of cobalt in the

samples of mango and apple fruit was detected greater than all the vegetable samples whereas other fruit samples indicated no special difference with vegetable samples. The concentration of cobalt in the peel samples of peach and banana were found lower than all fruit samples. Permissible limit for Co is 0.05-0.1mg/kg as set by ATSDR. The concentration of Co cross the safe values in all the samples which leads to the toxicity of cobalt. The concentration of Co in these samples is between 0.3 to 0.5 ppm as shown in figures 5 & 6.

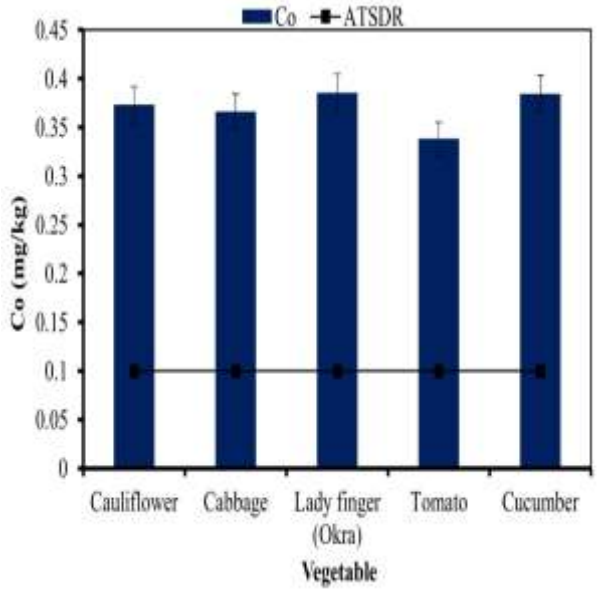

Figure 5: Concentration of Cobalt in Vegetables

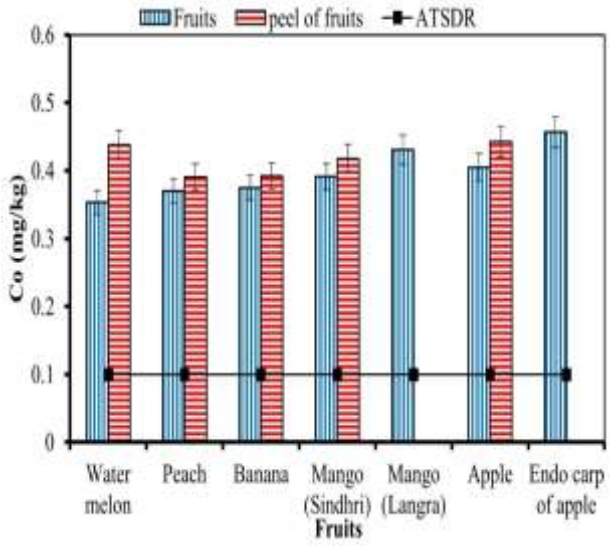

Figure 6: Concentration of cobalt in fruits and peels of fruit

Manganese: It is an essential trace element which act as Anti-oxidant and play important role in the metabolism of carbohydrate, Protein and cholesterol processing. The daily intake of Mn is 2-5mg/day; it is stored in bones, skin, Liver and kidneys [19]. Fruits, vegetables, legumes, seeds and whole grains are good source of Mn. Its deficiency causes Weak bones, Painful joints, Osteoarthritis (Tired blood) and weight loss. Just 12-20 mg of Mn is present in the body of human. The concentration of Mn in all samples of Fruits and vegetable is below than permissible limit (9500 ppm) set by WHO/FAO (Figures 7 & 8).

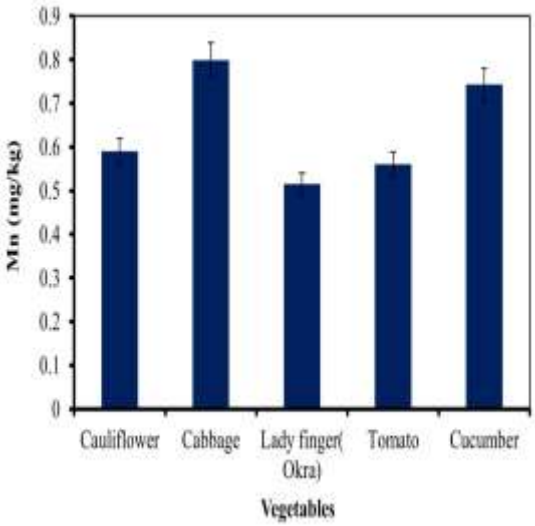

Figure 7: Concentration of manganese in vegetable samples

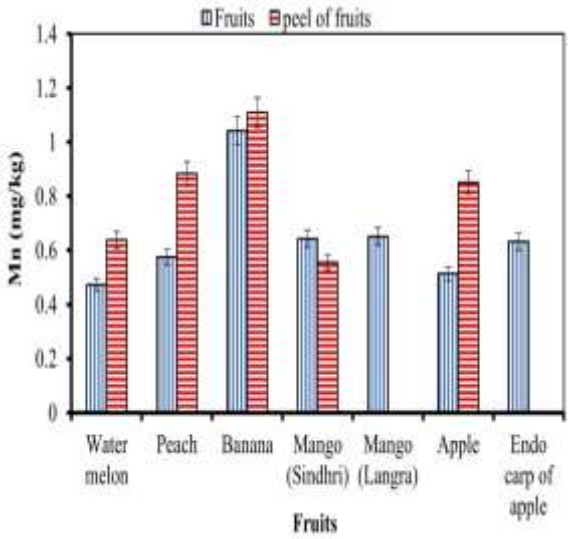

Figure 8: Concentration of manganese in fruits & peels of fruits samples

Cadmium: It is a trace heavy metal it is found as impurity in many products such as Phosphate fertilizers, detergents and petroleum products. Acid rain and industrial wastes increase the Cd concentration in soil.The intake of Cd contaminated vegetables results into stomatch pain, Dirhea, Vomiting, Bone fracure and failure of central nervous system and reproductive failure [7]. The concentration of Cd is found greater in the peels of Fruit than their Fruits which in turn were detected greater than vegetables (Figures 9 & 10). The permissible limits of Cd (0.1 ppm) and (0.3 ppm) are set by WHO/FAO and European Union (2006) respectively. The concentration Cd in all samples is slightly above the safe values set by WHO/FAO and within the safe value set by European Union (2006).

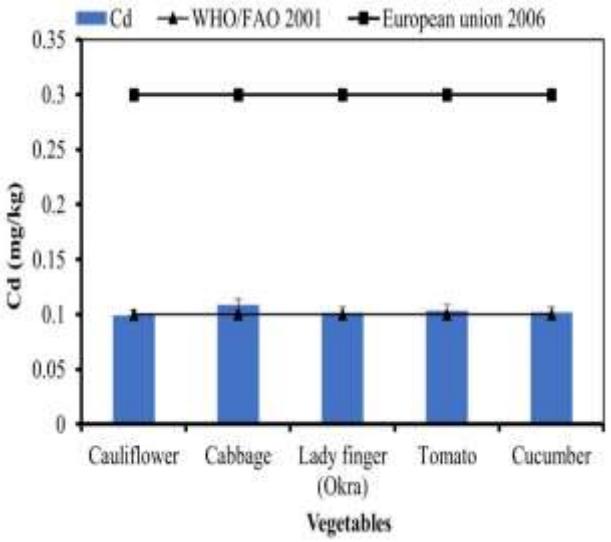

Figure 9: Concentration of cadmium in vegetable samples

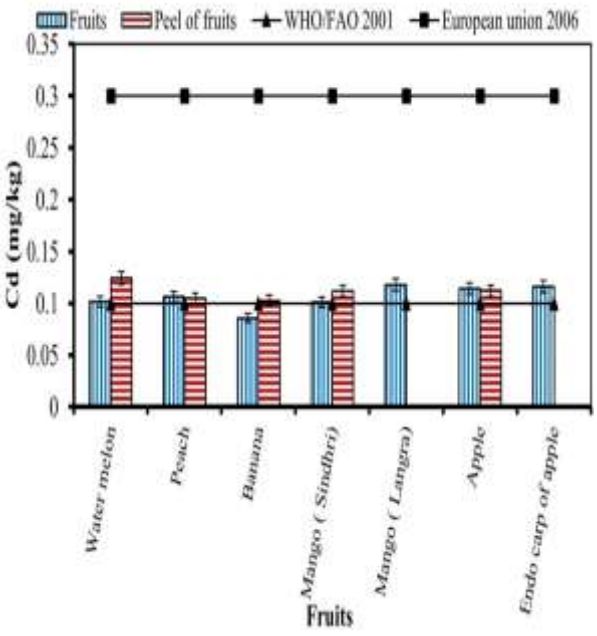

Figure 10: Concentration of cadmium in fruits & peels of fruits samples

Copper: It is a vital trace heavy metal. Copper is required for the production of energy in cells. It approximately makes 9 gram of body weight; it is found in enzymes involve in oxygen reactions. Copper is involved in metabolism of estrogenic which is required for Women's fertility to maintain pregnancy, deficiency of copper effect thyroid function, central nervous system (CNS) disorder & hair abnormalities. Toxicity of Cu causes deficiency of Haemoglobin, erythrocytes level, cancer and death [17]. The concentration of Cu in the peels of Fruits were greater than the Fruits samples which in turn were found greater than the vegetables as shown in figures 11 & 12 respectively. The level of Cu in all the samples of fruits and vegetables were observed below than the standard value (40 ppm) given by WHO/FAO.

Nickel: It is a trace heavy metal and present in many enzymes in microorganisms, Plants and humans. It plays important role in physiological processes, it acts as a co-factor in Iron absorption from intestine. It also involve in immune system, excess of Ni cause decrease in body weight, increased heart and decreased liver weight [20].

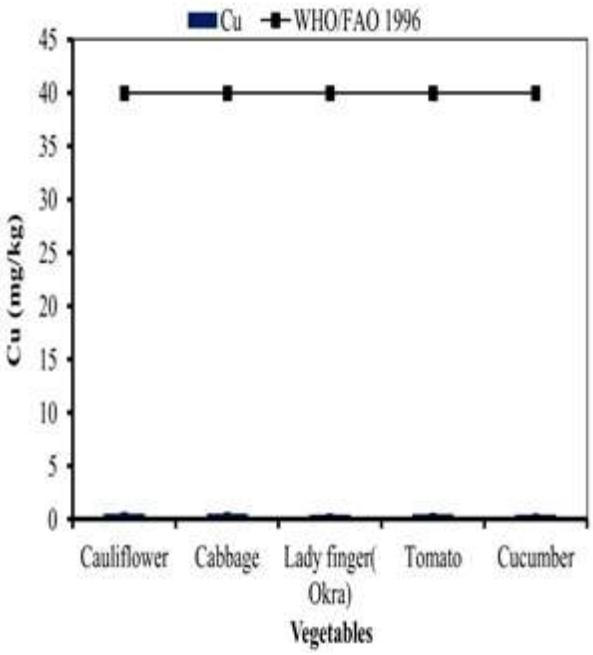

Figure 11: Concentration of copper in vegetables samples

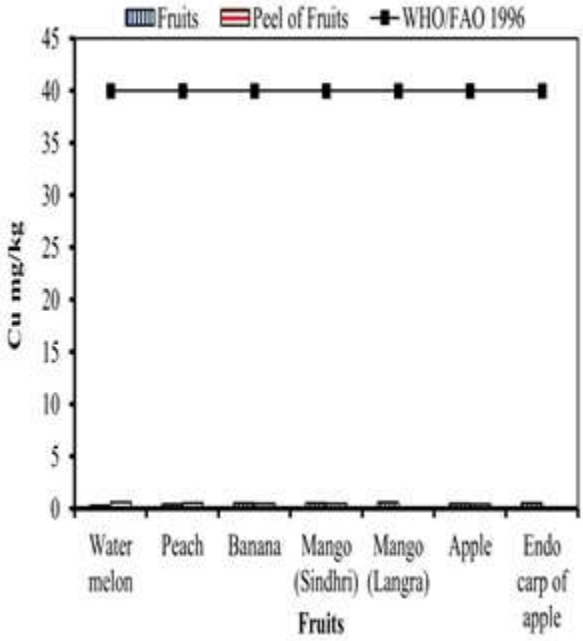

Figure 12: Concentration of copper in fruits & peels of fruits samples

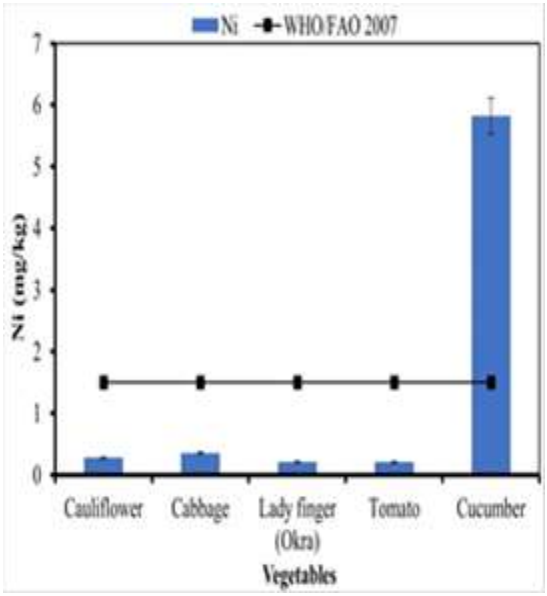

Figure 13: Concentration of nickel in vegetables

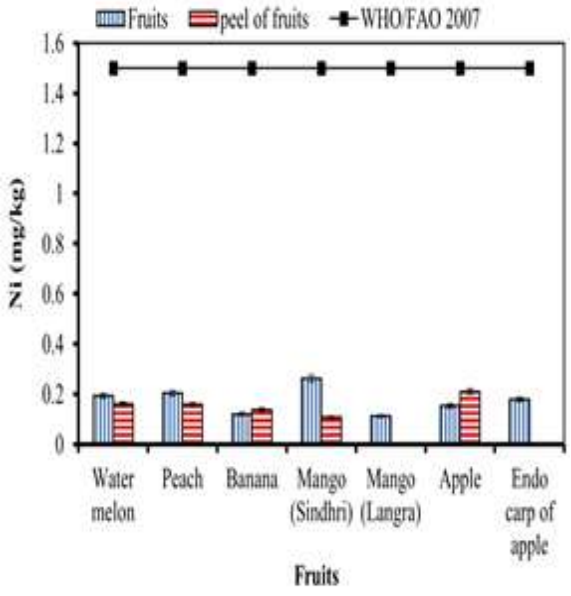

Figure 14: Concentration of nickel in fruits and peels of fruits samples

Table 5: Standard values of heavy metals in ppm.

Heavy metals	Standard values (ppm)	Organizations
Fe	425	WHO/FAO (2001 & 1994)
Pb	0.3	WHO/FAO (2001 & 1994)
	0.2	China food hygiene standard
Co	0.05 – 1	ATSDR (1994)
Mn	500	WHO/FAO (2001 & 1994)
Cd	0.1	WHO/FAO (2001 & 1994)
	0.3	European Union (2006)
Cu	40	WHO/FAO (1996)
Ni	1.5	WHO/FAO (2007)

4. Conclusions

The concentrations of Fe, Mn and Cu were below the permissible limits in all samples of fruits, peel of fruits and vegetables. However, the Concentration of Pb crossed the safe values in all the samples of fruits and vegetables set by WHO/FAO and CFHS (China food hygiene standards), except lady finger and cauliflower in which concentration of Pb was in the range of standard values. On the other hand, the concentration of Co also crossed the permissible limit in all samples of fruits, peel of fruits and vegetable which leads to toxicity. It is due to the contaminated water used for watering them. Similarly, the concentration of Cd is above the permissible limit in all samples of vegetables, fruits and peel of fruits given by WHO/FAO except banana fruit. However, the concentration of Cd was found within safe limit set by European Union (2006). The concentration of Ni was detected below the permissible limit (1.5 ppm) in all samples of fruits, peel of fruits and vegetable except cucumber which showed higher concentration (5.8191 ppm) of nickel than permissible limit. It is concluded that all the vegetables samples and fruits samples are badly contaminated with heavy metals Pb, Co, Cd and Ni which has hazardous effect on Human health.

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References

[1] Salvatore, M. D.; Carratù, G.; Carafa, A.; "Assessment of heavy metals transfer from a moderately polluted soil into the edible parts of vegetables"; J. Food Agric. Environ. 7, 683-688, 2009.

[2] Hellen, L. E.; Othman, O. C.; "Levels of selected heavy metals in soil, tomatoes and selected vegetables from Lushoto District-Tanzania."; Int. J. Environ. Monitor. Anal. 2, 313-319, 2014.

[3] Khan, H.; Khan, S.; Khan, N.; Ali, I.; Achakzai, A. B.; "Physicochemical and spectroscopic elemental analysis of ground water in thickly populated and industrial area of Quetta valley Pakistan"; Al-Nahrain J. Sci. 22, 18-25, 2019.

[4] Ibrahim, L. H.; Abed, S. A.; "Accumulation detection of some heavy metals in some types of fruits in the local market of Al-Diwaniyah City, Iraq"; Rasayan J. Chem. 10, 339-343, 2017.

[5] Ismail, F.; Anjum, M.; Mamon, A.; Kazi, T.; "Trace metal contents of vegetables and fruits of Hyderabad retail market"; Pak. J. Nutr. 10, 365-372, 2011.

[6] Mehari, T. F.; Greene, L.; A'ja, L. D.; Fakayode, S. O.; "Trace and macro elements concentrations in selected fresh fruits, vegetables, herbs, and processed foods in North Carolina, USA"; J. Environ. Protec. 6, 573, 2015.

[7] Habib, H. R.; Awadh. S. M.; Muslim, M. Z.; "Toxic heavy metals in soil and some plants in Baghdad, Iraq"; Al-Nahrain J. Sci. 15, 1-16, 2012.

[8] Randhawa, M.; Ahmad, G.; Anjum, F.; Asghar, A.; Sajid, M.; "Heavy metal contents and their daily intake in vegetables under peri-urban farming system of Multan, Pakistan"; Pak. J. Agric. Sci. 51, 2014.

[9] Volpe, M.; La-Cara, F.; Volpe, F.; De-Mattia, A.; Serino, V.; Petitto, F.; Zavalloni, C.; Limone, F.; Pellecchia, R.; De-Prisco, P.; "Heavy metal uptake in the enological food chain"; Food Chemistry 117, 553-560, 2009.

[10] Igwegbe, A. O.; Agukwe, C. H.; Negbenebor, C. A.; "A survey of heavy metal (lead, cadmium and

copper) contents of selected fruit and vegetable crops from Borno State of Nigeria"; Res. Inv. Int. J. Eng. Sci. 2, 1-5, 2013.

[11] Elbagermi M. A.; Edwards, H. G. M.; Alajtal, A. I.; "Monitoring of Heavy Metal Content in Fruits and Vegetables Collected from Production and Market Sites in the Misurata Area of Libya"; ISRN Analytical Chemistry , 1-5, 2012.

[12] Mohod, C.V.; "A Review on the Concentration of the Heavy Metals in Vegetable Samples like Spinach and Tomato Grown Near the Area of Amba Nalla of Amravati City"; Int. J. of Innov. Res. Sci. Eng. Technol. 4, 2788-2792, 2015.

[13] Farooq, M.; Anwar, F.; Rashid, U.; "Appraisal of heavy metal contents in different vegetables grown in the vicinity of an industrial area"; Pak. J. Botany 40, 2099-2106, 2008.

[14] Khan, S.; Cao, Q.; Zheng, Y.; Huang, Y.; Zhu, Y.; "Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China"; Environmental pollution 152, 686-692, 2008.

[15] Karpiuk, U. V.; Al-Azzam, K. M.; Abudayeh, Z. H. M.; Kislichenko, V.; Naddaf, A.; Cholak, I.; Yemelianova, O.; "Qualitative and quantitative content determination of macro-minor elements in Bryonia alba L. roots using flame atomic absorption spectroscopy technique"; Advanced pharmaceutical Bulletin 6, 285, 2016.

[16] Omer, M.; "Assessment of some heavy metals in fruit from local market in Khartoum state"; 2013.

[17] Islam, E.; Yang, X-E.; He, Z.; Mahmood, Q.; "Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops"; J. Zhejiang Univ. Sci. B. 8, 1-13, 2007.

[18] Hellen, L. E.; "Levels of Selected Heavy Metals in Soil, Tomatoes and Selected Vegetables from Lushoto District-Tanzania"; Int. J. Env. Monitor. Anal. 2, 313, 2014.

[19] Tsugutoshi, A.; "Copper deficiency and the clinical practice"; Trace Elements 365, 2004.

[20] Das, K.; Das, S.; Dhundasi, S.; "Nickel, its adverse health effects and oxidative stress"; Ind. J. of Medic. Res. 128, 412, 2008.