EVALUATION OF HEAVY METALS PRESENT IN SOME SELECTED VEGETABLES AT QUETTA CITY SUBURBS IN BALOCHISTAN.

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ABSTRACT: *The objective of this experiment work is to determine the level of heavy metals Lead, Cadmium, Nickel, Chromium, Copper, and Zinc in some selected vegetables in the proximity of Quetta city, irrigate by wastewater and clean water of Tube well. Plant samples were exclusively collected from the same area and subjected to conventional analytical procedure. The results showed that the majority of samples of cabbages and Spinach irrigated by waste water drains of the city were found contaminated beyond the medically permissible limits.*

Key words: Heavy Metals, Atomic Absorption Spectroscopy & Drinking Waters

1. INTRODUCTION

Balochistan province of Pakistan produces different vegetables on a large scale. In 2002 and 2003, the area under cultivation estimated for vegetable production increased from 13359 to 14026 hectares and yield risen from 144741 tons to 173683 tons. According to the reports from various resources, the area for cultivation was increased by five percent and the yield by twenty percent. In this province, the total area used for growing vegetables was 14026 hectares producing 17383 tons of vegetables. Thus the total contribution to vegetables production is in the range 62.90% and 70.43%. Because of scarcity of water, the trend of farmers changed from the fruits to vegetables growth. The drought in 2001 the yield of fruits dropped by fifty-seven percent and twenty-three percent of trees were affected because of the shortage of water in Balochistan.

The cabbage is a green leafy plant that grows as a seasonal vegetable crop and closely relates to crops like broccoli, cauliflower, and Brussels which is the wild field cabbage. The cabbage heads commonly range, on the average, from 0.5 to 4 kilograms and found in green, purple and white colors. The red and green colors of cabbage are generally seen mostly in real. Cabbage is a multi-layer vegetable. Cabbage in summer grows more rapidly than the winter season.

According to the report of the food and agricultural organization of the United Nations, the worldwide production of cabbage and other brassicas in 2011 was estimated to be sixty-nine metric tons. Majority of these crops grows in China and popularly known as Brassica vegetable. Cabbage is the vegetable and made for cooking and a source of vitamin k and vitamin c.

The cabbage plant is shown in figure 1 below**:**

Fig. 1: The general image of the plant of Cabbage (*Brassica oleracea* or variants)

The cabbage is the plant of the genus Brassica and mustard family. Different vegetables are considered cultivars of B. Oleracea, includes broccoli, green collard, broccoli sprouting and kohlrabi and all of these obtained from cabbages wild. The species available presently have been evolved after thousands of years of experimentation, showing, different characters in cultivars like big heads of cabbages, big leaves of kale and bulky stem with flower bud for broccoli [1&4].

The spinach (*Spinacia Oleracea*) is the flowering plant in the family Amaranthaceae grown in Western and Central Asia.

Spinach is a seasonal plant grown in the winter and its growth on the averages is about 30 cm. The leaves of the spinach are triangular, 30 cm long and 15 cm broad. When the plant of spinach reaches its maturity stages, the seeds appear in its flowers.

The general image of the plant of Spinach (*Spinacia oleracea*) is shown below in Fig.2*:*

Fig. 2: The general image of the plant of Spinach (*Spinacia oleracea*)

The evidence of using spinach in medicines was recorded stems back to the 10th century in Arab countries. After in 12th-century spinach originates in Spain and called chieftain of leafy green [8]. The spinach was too used in special cases by Ibn e Ajjaj in the 11th century [9].

The sewerage and wastewater in the cities has been a major source for irrigating vegetable crops for long with the advantage of containing .more nutrients and organic matters. Most of the cities and towns municipality sold the water of sewerage to generate income. The wastewater from industries in suburban areas, when mixed with culverts and drains, contributes to pollution hazards for the planation. This mixed contaminated water at the same time releasing a bad unpleasant smell in the atmosphere intolerable for the surrounding population. The experiment was carried out in Faisalabad that yielded results showing the presence of harmful metals when the plantation irrigated by wastewater [10-11]. Jaffer *et al*. [12] stated that the high concentration of heavy metals was found in aquatic life. Effluents drained by industries in Korangi area and discarded in River Malir eventually polluting the Arabian Sea damaging large scale the sea food sources for human consumption.

Therefore, it was very important to note that the effluent mixed with wastewater used in the area of Korangi for the irrigational purpose be restricted for vegetables and other plantations. Therefore this study was carried out in hands to calculate the concentrations of Copper, Zinc, Iron, Cadmium, Nickel, Lead and Chromium in irrigational water in plants and soil.

The pollution of the environment because of the natural occurrence of volcanic eruption is another notable hazard. Nowadays, the rapid growth in innovation technologies, the chemicals emitted is a potential source of environmental pollution around industrial towns and villages. The release of toxic chemicals in environments is a big health hazard for living beings which through ecological cycles reach in oceans, soils, and foods [13]. The contamination of the soil where the vegetable and plants are grown affects the peoples and animals [14-15] .

The various growing methods are used by the growers to increase the yield of the crop and one such method is the fertilizers and animals dung to the soil. The different toxic in the soil affects the quality of crop and these elements directly or indirectly affect the production and alarming the needs of food supply [16]. Furthermore, the plant acts as vehicles to transfer these elements in the chain of food [17]. The metals which have higher specific gravity than 5 gram/cm^3 are called the heavy metals and most of the metals are not degradable and exist in the ecosystem [18]. The living organisms need a prescribed quantity of elements like iron, lead, cobalt, and chromium while above this amount it is otherwise very damaging for human health. The contamination of plants and vegetables is most common, resulted in the usage of untreated water for irrigation, released by industries, vehicles and different types of machinery to the soil [18]. The discharge of sewerage and waste of animals are total sources of heavy metals that contaminate the soil and plant [18]. The amount of metal contents founds in surface water by wastes and garbage. Furthermore, the metal finds its ways by leaching in the soil where the plant can contaminate the food chain [13]. This conclusion for some plants represents a seriously harmful when used as food [19].

The plants do not absorb the greater amount of heavy metals, and the quantity which they absorb depends upon the specie and the kind of plants, the chemical compositions of soils, the amount of heavy metals and the temperature of the soil. It is very necessary to take heavy metals in it which is very breakthrough for human beings. The intake of heavy metals in greater quantity through contaminated vegetables produces harmful diseases [20]. Duruibe *et al.* [21] reported that the harmful effects of heavy metals depend on the concentrations and oxidation of heavy metal.

The heavy metals like copper, cobalt, zinc, iron, and manganese at lower concentrations are very significant metals for enzyme activity and biological processes. The other metals like cadmium and mercury are very dangerous even at lower concentration. [22]. The food chain contaminated with heavy metals becomes the latest problem due to potential accumulations in biosystems via contamination of water, soil and air [23]. Continuous consumption of food, containing Cd, by humans cause the lives of animals and peoples [17]. The high level of contamination of food with cadmium effects of renal and pulmonary systems [24]. The greater amount of Pb causes the failure of kidney, reproduction, joints and cardiac issues [25].

The studies of Uwah *et al*. [26] also concluded that the amounts of heavy metals if found in spinach leave a trail of .harmful effect. This study also tells that the heavy metals are founds in roots and leaves of different vegetable crops in Nigeria. The other studies revealed that some vegetables like spinach, groundnut, and bean in Gwoza contain the amount of different heavy metals like cobalt, chromium, lead, and iron in different concentrations because of intensive and various growing activities like fertilizer applications and irrigation with wastewater in the region.

Another study, Adefemi *et al*. [20] revealed that the amount of heavy metal like cadmium, cobalt, chromium, nickel, copper, iron, manganese, lead and zinc was found in different plants obtained from selected dumpsites in Nigeria and these results showed that the plants were greatly contaminated with heavy metals. Further studies tell that the cobalt was actively transported to the leaves of the vegetables as well as in the roots of the plants. The studies are carried out on lead which is very harmful to the peoples founds in the ranges of 5.02 to 8.80 milligrams per kg in L. Sativa and greater concentrations of 16.67 milligrams per kg in H. Sabdarifa. They concluded that these values were higher than the maximum permitted level proposed by FAO/ WHO guidelines and that all the vegetables studied were contaminated by Cd and Pb thus rendering the plants toxic to consumers.

The determination of the amount of heavy metals is very significant while consideration of the necessity of vegetables to the health of human beings because peoples like to eat vegetables for making their life healthy. A vegetable plays an important role in human health because of vegetable shave proteins, carbohydrates, vitamins and some amount of minerals [29]. The levels of the heavy metals were also determined in the soil where the vegetables are cultivated.

The heavy metals are founds in soil by naturally and as of humans activity. The heavy metals are very dangerous for human life because they cause cancer, illness, and blindness [31]. The heavy metals pollution of aqueous stream, soil and sediments are the main environmental issue. Most of the developing countries have concluded that heavy metals contaminated wastewater had been used for irrigational purposes [32-36]. The all of heavy metals at higher concentrations have harmful effects and regard as environmental pollutants [38-39]. The vegetables like cabbage grown by using wastewater which takes a higher amount of heavy metals to cause health issues to the users [40].

As a sample, the plant brassica juncea was chosen for rhizo filtration which contains the Pb and many heavy metals. Furthermore, the various members of this family shown to have an unnecessarily higher concentration of heavy metals in the roots and stems [41]. The pollution of subsurface water and soil with heavy metal creates atmospheric issues and threats to the health of peoples and animals [42]. The usage of plants in the environment cleaned like harmful metals guaranteed a green and clean atmosphere with the cheapest cost. The main aim of this study was to counter the concentrations of heavy metals in wastewater and soil from the nagodi mines area and their translocations in lactuca sativa, brassica oleracea, l. var capitata and daucus carrota var sativa. Also evaluation and comparison of the bio accumulation of heavy metals in the grown vegetables in soil with using nagodi mine waste water.

Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes, etc. [45]. The soil is polluted via applications of chemical fertilizers such as zinc and phosphate [46]. The heavy metals accumulate in the soil is the big concerns in agricultural production because of its huge effects on the quality of food, growth of crop and healthy environment [47-49].

The plant species have varieties of capacity in removing heavy metals so there are many reports of different plants that accumulate heavy metals [48]. Taking of metals from the soil depends upon the various characteristics like soluble contents, pH of the soil, plants specie, fertilizer and the type of soil [49]. The vegetables mostly which have leaves accumulate a greater amount of heavy metal than stem and fruit [50]. The roots and leaves of herb plants retain high concentrations of heavy metals instead of stem and fruit [51].

Mostly there are minor works carried out on heavy metals contents at various stages of vegetable growth and more of the works were carried out to found metal contents in edible parts of the vegetables. Furthermore, this work was carried out (a) To investigate and compare the level of concentrations of heavy metals like lead, cadmium, nickel, cobalt, chromium, copper and zinc at various vegetables which irrigate by wastewater and pure water to analyze the concentration of heavy metals contents by other vegetable species.

2. EXPERIMENTAL

Samples and sampling

The vegetable samples root and leaves of spinach and lettuce and soil of the areas were obtained in Oct. 2015 from vegetable fields in Quetta City, Mahalla Pushtun Bagh (Spinny Road), Spinny Road Ganj and Jangle Bagh. In these areas vegetables grown with the usage of fertilizers, animal dung and irrigated by wastewater. Specimens were obtained by using the methods given by Radojevic and Bashkin [17]. Samples were collected and transported to the laboratories in polythene bags for analysis.

Digestion and analysis of samples

The soil and slice vegetables and their specimens were dried on 105^{o}C for a day in the oven till the samples were broken down [52]. Just one part with two grams of dried sample disaggregated and sieves and specimens placed in 100 cm^3 and digest with 15 cm^3 concentrates with nitric acid at a 550^o C for three hours and filtered in 100 cm^3 volume of flask [52 & 18]. The level of iron, cobalt, lead, and chromium in vegetables and the specimens of soil were investigated by sp 1900 AAS with air acetylene burner. The formula of heavy metal concentration in the vegetables and soil specimens areas:

$$\text{Concentrat} = \frac{\text{Concentrations (milligram/Liter)} \times V}{M}$$

where:

V = final volume 100 cm^3 of solutions after digestions

M = initial weights (2 grams) of specimen calculated

Transfer factors for heavy metals from soil to Vegetable

Ionic cases of the soils sample were compared with vegetable specimens then transfer factors are the ratios of the concentrations of heavy metal in the plants to the concentrations of heavy metal in the soil. The heavy metal transfer factor for every metal describes by Harrison and Chirgawi by this equation:

Transfer Factor=Ps/St (milligrams per kg dry weight) (2)

where:

Ps = plant metal contents

St = total heavy metals content

Data analyses

Data were obtained by three parts and data were subject to the statistical test of significances by analysis of variances and the student's tests at p is less than 0.05 to assesses a couple of results in the soils and vegetables and these results were significantly considered less than 0.05, and total data were analyzed statistically by software.

3. RESULTS AND DISCUSSION

The levels of heavy metals calculated in the vegetables and soils are shown in Tables 1 and 2 and fig. 3 and 4.

Table1: Level of HMs (milligram per kg) in vegetables irrigated by clean water of Quetta City.

S.NO	Name of vegetable	Pb	Cd	Ni	Co	Cr	Cu	Zn
1	Cabbages (Spinny Road Ganj}	0.36	0.002	0.35	4.2	0.04	0.06	1.5
2	Spinach (Pushtun Bagh}	0.24	0.041	0.656	5.2	0.03	0.7	0.045

The HMs have greater importance in eco chemistry and ecotoxicology due to their toxic at less level and tendencies to accumulates in people's organisms [54].

The high concentration of lead in the vegetables can attribute their locations and proximities to the highways. The samples of vegetables calculated from the highways had high (p is less than 0.0001) lead concentrations than those taken from a Mahalla Pushtun Bagh (Spinny Road), Spinny Road Ganj and Jangle Bagh, Quetta City.

Lead is very harmful to the plants and plants can accumulate a greater quantity of lead without changing their appearance and production. A different plant accumulates a higher level of lead which is greater than the range of max. limit [55]. For conducting this study, specimens were obtained from Jangle Bagh, Quetta City, a higher amount of lead was found in cabbage and spinach. Proximity with highways emits lead from vehicle exhaust gets deposit on the exposed vegetables. Lead pollutions have been shown to commensurate with densities of vehicles and populations.

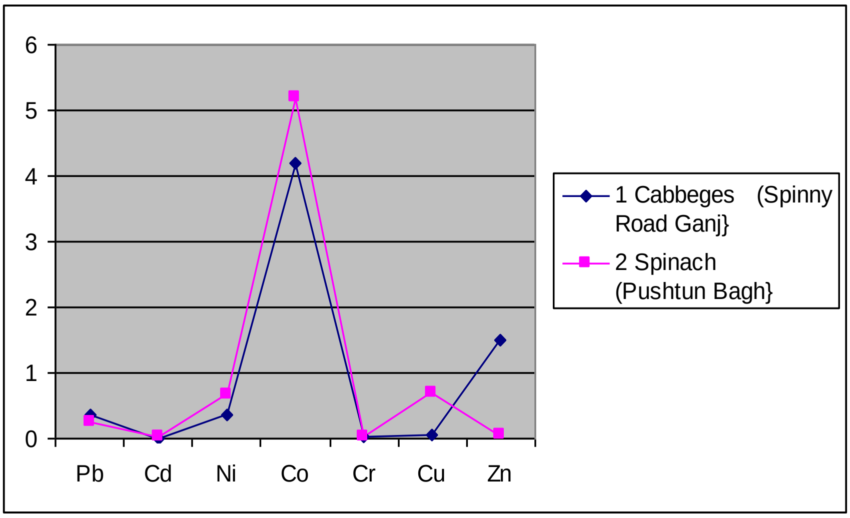

Fig. 3: Level of HMs (milligram per kg) in vegetables irrigated by clean water of Quetta City.

Table 2: Levels of HMs (milligrams per kg) in vegetables irrigated by wastewater of Quetta City

S.NO	Name of vegetable	Pb	Cd	Ni	Co	Cr	Cu	Zn
1	Cabbages (Jungle Bagh}	1.68	0.2	0.42	6.1	0.8	0.1	2.86
2	Spinach (Jungle Bagh}	1.53	0.55	0.75	6.3	0.1	0.8	0.09

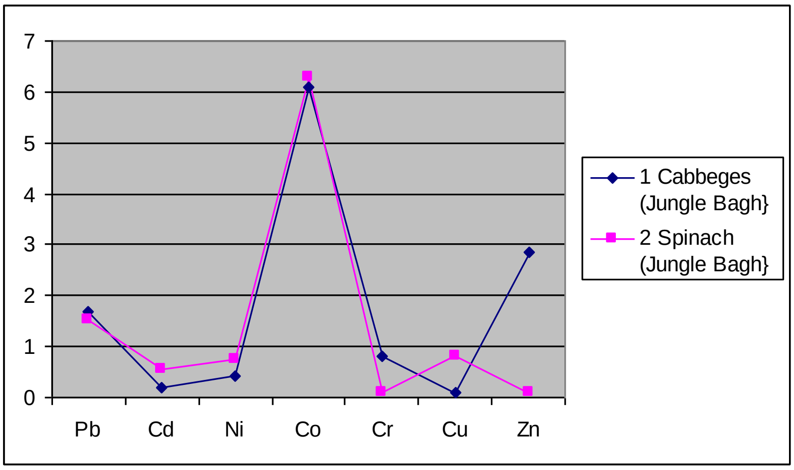

Fig. 4: Levels of HMs (milligrams per kg) in vegetables irrigated by wastewater of Quetta City

The consumption of vegetables contained heavy metals results in health issues. The greater amount of lead founds in bones and teethes [56]. The presence of lead in the body of human beings causes weakness in the wrist and fingers. The presence of lead in the bodies of human beings causes renal problems, pregnancy problems, muscle weakness and reproduction problems [57].

The results of this study concluded that the presence of lead was shown in all the vegetables and based upon the value of a lead in various vegetables can be taken if 80 grams of these inspired a day and six milligrams per kg recommended according to the standards [58].

This work resulted that the continuous consumption of vegetables is very harmful and hazardous results. Environmental monitoring can be done for heavy metals regularly to evaluate the lead toxicity in vegetables from the areas

The HMs accumulates and translocation varies from plant to plant and metals to metals not follow the exact patterns. The genotype effects, environmental effects and the effects of their interactions greatly affect the heavy metal uptakes in crop genotype [59-62]. Furthermore, the heavy metal in soil occurs in complex form due to interlinkage with the number of physicochemical forms that in turn influences their availabilities [63]. The plants taking up the heavy metals from the soils with various reactions like adsorptions, ion exchange and precipitations with others [64]. The relative fewer concentrations of cadmium accumulate in brassica oleracea l. var capitata and lactuca sativa which describes the presence of zinc in the vegetables. Many professionals and researchers identify that the occurrences of zinc inhibit cadmium adsorptions and thereby causes fewer cadmium accumulations in plant [65 & 57]. These results indicate that the vegetable accumulates some quantity of zinc. Cadmium and Zinc may be considered chemically the same compounds due to having the same ion structures and electronegativity which influence each other in plants uptake and accumulate while they play other roles in the plant's metabolisms. The Zn is the micro nutrients while cadmium is harmful and doesn't play roles in plants [66]. Furthermore, these both have the different ion radii (Zn^{2+} = 0.074 nm and Cd^{2+} = 0.0979 nm); this variation plays important role in the plants selection for Zn [67]. The result reveals that the average concentrations absorb in the parts of the vegetables. The chromium and zinc are the compounds having the same geochemical and environmental parameters; and the chemical similarity leads to interact in two metals among the uptake of plants, transportation, and accumulation in the different parts of the plant [68]. Furthermore, in general, the acceptable value of zinc in the soils and plants plays significant roles in the cadmium accumulate in crops plant. The iron concentrations reduce the uptakes of cadmium [70]. Order of zinc accumulates in spinach and spinach which are given in tables 1, 2 and 3. The average concentrations of zinc in vegetables irrigate with taps water than the treated water in cabbage. The zinc is the micronutrients important for plant metabolisms while vegetable absorbs when physiological function shows the indication that the speedy growth rates are taken into the controlled than those which grow in the soils from mine areas irrigate with wastewater. Hence it may be the result that the greatly lower accumulations of cadmium. The higher concentrations of nickel found in cabbage can attribute to the microbiological consortiums in the plant's root which excretes organic acid which facilitates the absorptions and accumulations of nickel cabbage. Context of this statement that the many microorganisms excrete with compounds that increase bioavailability and enhances the roots absorptions of important metals like nickel [71]. Cu is the most important micronutrient which plays a significant role in plant development. In the study Cu accumulated in various parts of the crops and the orders of accumulations of Cu in cabbage are greater than the spinach. The average concentrations of Cu in vegetables were very low than the recommendations of FAO in vegetables 73.3 milligrams per kg and the lower concentrations of chromium were found and the orders of chromium absorptions are found greater in cabbage than spinach and total concentration are shown in table 2 according to FAO standards. Pb absorbed greatly just a plant that is used in the experiments. The average concentrations of lead accumulate greater than the limit which is 0.005 milligrams per kg. The higher mobilization and uptaking of lead were found in the more acidic soils. Many professionals and researchers stated that with a lower pH than the higher potentials to be up to take and Translocate by the plant [72]. The presence of lead in the soils has the greater potential for absorptions while lead is not capable to translocate the plant from growing soils. From this statement that the lead is greatly adsorbed by sediment particles and too difficult to be Trans locate [64]. Limited steps for lead accumulations are the great distances translocations from root to shoot [73].

4. CONCLUSION

The heavy metals contents in various leaf vegetables differ greatly and the contents vary with duration of harvest and mature stage of the crop. The chromium and lead in vegetables in this work were noted lower but the lead was greater than the limit given by the standards. Hence the usage of contaminated water for growing vegetables can create harmful contaminations of metal pollution. The consumption of vegetables as food cannot constitute harmful ingredients for human health in this study.

5. RECOMMENDATIONS

● The usage of wastewater in vegetable crops can be checked and treated to reduce the HMs level.

● The awareness is required to neglecting the fruit and vegetables in areas where the heavy concentrations of Pb found and also make the rules and regulations to avoid the cultivation of vegetables and fruits in the areas where Pb concentrations are found.

● Furthermore, the studies will be carried out to collect more information about the ages of plants which effected by HMs.

● Awareness must be required to using the crops and vegetables which have concentrations of HMs which cause health issues in human beings.

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