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METALS UPTAKE BY WASTEWATER IRRIGATED VEGETABLES AND THEIR DAILY DIETARY INTAKE IN PESHAWAR, PAKISTAN

POBIERANIE METALI PRZEZ WARZYWA NAWADNIANE ŚCIEKAMI I ICH DZIENNE STĘŻENIE W DIECIE LUDNOŚCI PESZAWARU, PAKISTAN

Abstract: Vegetables are important source of nutrients for human body. Wastewater irrigation may lead to contamination of these vegetables and cause possible health risk. In the present study impact of waste water irrigation on metals uptake (Fe, Mn, Ni, Co, Zn, Cd, Cr and Pb) by five commonly consumed vegetables (radish, cabbage, lettuce, cauliflower and spinach) grown in the suburbs of Peshawar were investigated using AAS (Atomic Absorption spectrophotometer). The uptake and accumulation of metals for vegetables irrigated with wastewater were significantly ($p < 0.05$) higher than tube well irrigated vegetables and permissible limits of WHO/FAO. Among the edible parts of vegetables maximum accumulation of Mn, Pb and Cd occurred in radish followed by Ni and Fe in spinach while Cr and Zn were high in cauliflower and cabbage. The estimated daily intake of metals (DIM) revealed that at present the consumption of studied vegetables were under the tolerable limits of (US-EPA, IRIS), however intake of metals in waste water irrigated vegetables were significantly high and can cause health hazards in the long run.

Keywords: heavy metals, vegetables, daily intake of metals, wastewater, bioconcentration factor, Peshawar

Introduction

Vegetables are important part of human diet. They provide many essential nutrients to human body for normal growth and development. It can also prevent various toxic substances during digestion and support better health such as minimizing the risk of colorectal cancer and other diseases [1]. However, nutritional quality and food safety measures should be kept in mind when recommending vegetables for human consumption because they contain both essential and non essential minerals [1-3].

Wastewater irrigation is a prevalent practice for many years in most develop and underdeveloped countries of the world, such as Germany, France, India, Pakistan [4-8].

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Industrial effluents and municipal wastewater in suburban ecosystem is an ultimate source for irrigation, because of their availability, problems of disposing and fresh water scarcity. It is evident that using wastewater for irrigation significantly increase heavy metals content in the soil [9], thus wastewater irrigation can be both beneficial as well as harmful in agricultural sector [10]. Wastes utilization in agriculture provides an economical way to disposed off of these materials by producing little environmental effects [11]. Wastewater can be used as an important water resource and considering their beneficial aspects that it can add organic matter and plant nutrients to soil [12]. However, it causes the buildup of heavy metals concentrations in agricultural soil which not only contaminate soils, but also deteriorate safety and quality of food [13].

Heavy metals are detrimental to human health because they have the capability to accumulate in various parts of the human body. They may have adverse health effects even in low concentrations [14], because they are persistent in nature and cannot be degraded [15]. Many of the food plants can easily accumulate heavy metals and result in an increased quantity of these metals in the farm’s produce [16, 17]. Contaminated soils are one of the major sources for food chain translocation of heavy metals and further their intake through consumption of contaminated vegetables and other crop plants which ultimately poses health risks for human health [17-19]. Furthermore, the intake of metals (Cu, Cd, Ni, Pb, Zn, etc.) can have antagonistic effect on some of the essential nutrients inside the body, which results in the depleted immunological defenses, intrauterine growth retardation (caused by Al, Cd, Mn and Pb), psychosocial dysfunctions, and abnormalities such as malnutrition and gastrointestinal cancer [19, 20].

Generally crop plant take up many essential nutrients and trace elements in a short period of time, therefore, the safety of vegetables has a concern for human health and attract more attention [12]. Some of the vegetable such as lettuce, spinach, radish and carrot, can easily take up heavy metals *eg*, Cu, Cd, Pb, Zn and Mn in their tissue. The uptake of these metals by plant is generally increased when they are grown on contaminated soils [21]. Studies related to health risk assessment of heavy metals in contaminated vegetables are being conducted in the developed world [22], however limited work is available in developing countries and need to be explored [23]. In Pakistan there is limited published data available regarding contamination of metals in vegetables grown in suburban environment [7, 24, 25].

The present study aimed at comparing heavy metals (Fe, Pb, Zn, Mn, Ni, Co, Cd and Cr) accumulation of some commonly consume vegetables (radish, cabbage, lettuce, cauliflower and spinach) in Peshawar city, Pakistan. Wastewater irrigation is a common practice in Peshawar city, where the households refuse and industrial effluents are directly discharged off in the irrigation system. In the current study impact of wastewater irrigation on uptake of heavy metal was also studied and compared with relatively clean source of irrigation. Furthermore, the bioconcentration factor of selected metals in the studied vegetables and their dietary intake for children and adults are calculated.

Materials and methods

Study areas

Peshawar is the capital and largest city of Khyber Pakhtunkhwa province of Pakistan with an area of 77 km^2 having more than one million population. The suburban part is mainly used for cultivation of vegetables and forage crops, which are transported later on to the city for human consumption and animal feeding. Whereas the irrigation source for these crops is a canal originated from Shalam River which also receives wastewater from a stream carrying industrial effluents from the nearby industrial zone is used for irrigation purposes due to the lack of public awareness [7]. Moreover these canals also receive the household wastewaters and disposals, which further multiply the hazards of contamination and risk for inhabitants.

Samples collection and handling

All the experimental work was carried out at the department of Agricultural Chemistry, University of Agriculture Peshawar, Pakistan. Five commonly cultivated vegetable like radish, cabbage, lettuce, cauliflower and spinach were collected from four different locations of Peshawar, Pakistan such as Bahadar Kalay, Phandu Payan and Pakha Ghulam, where wastewater is used for irrigation and Professor Colony (Malakandare Farm), where the source of irrigation is tube well water. Vegetable and soil samples were randomly collected from the farmer fields while the irrigation water was sampled from the water courses of the same fields from where the soil and vegetable samples were taken. All the samples were then transported to the laboratory immediately. The obtained vegetables were properly rinsed with tape water followed by double distilled water to remove any adhering pollutants and were cut with a stainless steel knife to separate them into roots, stem and leaves. These samples were then subjected to oven drying at 70 to 80°C to remove all the moisture and were grinded to make it in powdered form.

Digestion and preparation of samples

Vegetable samples were digested according to wet digestion method as described by Jan et al [7]. Briefly a sample of 0.5 g was digested using digestion tube by adding 1 cm^3 of $HClO_4$ and 4 cm^3 of HNO_3. When the content became clear samples were cooled and filtration was carried out using Whatman 42 filter paper. The filtrate was then diluted to 25 cm^3 with deionized water. A blank was also run performing the same steps without adding the sample.

Soil samples were digested by following the method of Sharma et al [26]. One g soil was transferred to a 250 cm^3 digestion tube containing 10 cm^3 concentrated HNO_3. The tubes were then boiled for 30 to 45 minutes. After oxidation, the samples were subjected to cool, 5 cm^3 of 70% $HClO_4$ was then added and the content was boiled again till the appearance of white fumes. The tubes were allowed to cool for some time and 20 cm^3 of distilled water was added and boiled again till the fumes disappear completely. The solution was then allowed to cool, filtered through Whatman filter paper No. 42. The filtrate was transferred to 25 cm^3 volumetric flask. The final volume was mark with deionized water. A blank was also prepared following the exact procedure without adding soil sample. Water samples were prepared by taking 50 cm^3 in a beaker and treated it with 10 cm^3 concentrated HNO_3. The solution in beaker was heated until 40 cm^3 volume remained. The solution was passed again through Whatman filter paper No. 42 and diluted to 50 cm^3 by adding deionized water. A blank solution was made in the similar way without adding water sample.

Determination of heavy metals

The entire chemicals used were of analytical grade. Double deionized water was used for sample dilution and reagent preparation. The selected heavy metals were analyzed using Atomic absorption spectrophotometer (Perkin Elmer model 2000, USA). Different working standards were made from Perkin Elmer standard stock solutions (1000 ppm) used for the determination of metals. The detection limits and wavelengths of the metals are shown in Table 1. For precision and accuracy of analytical work, the values of blank were subtracted from sample. Also quality control procedures were adopted to minimize contamination and enhance the reliability of data. Standards were run after every five samples, to ensure that the instrument is working properly. Data were recorded in triplicates.

Table 1

Detection limits and wavelength of each element used for AAS analysis

Metals	Wavelength [nm]	Limit of detection [$\mu g cm^{-3}$]
Ni	232.0	10.0
Cr	357.9	6.0
Cd	228.8	1.5
Pb	283.3	10.0
Zn	213.9	2.0
Fe	248.3	6.0
Mn	279.5	2.0
Co	240.7	5.0

Data analysis

Bioconcentration factor (BCF)

Bioconcentration factor (BCF) is the ratio of the elemental concentration in plant tissue such as, leaves, stem, root etc. and the "exchangeable" or potentially available portions of metals in rhizospheric soils. The BCF for edible part of vegetable was calculated with the following formula:

$$BCF = \frac{Cp}{Cs}$$

where Cp is the concentration of metal in edible part of vegetable [mg kg^{-1}] and Cs is the metal content in soil [mg kg^{-1}].

Daily intake estimates

The daily intake of metals (DIM) of various metals for children and adults were estimated using the following equation:

$$DIM = \frac{M \cdot K \cdot I}{W}$$

where M is the concentration of metals in plants [mg kg^{-1}], K is the conversion factor, I is the daily intake of vegetables, W is the average body weight. A conversion factor 0.085 was used to convert fresh weight of vegetables to dry weight as suggested previously by Rattan et al [27]. The body weights of average adult and child were assumed to be 73 and 32.7 kg, respectively [7], while average daily intakes of studied vegetable for adults and children were assumed to be 0.345 and 0.232 kg/person/day, respectively [28]. The triplicate data are compiled in terms of means and standard deviation (SD).

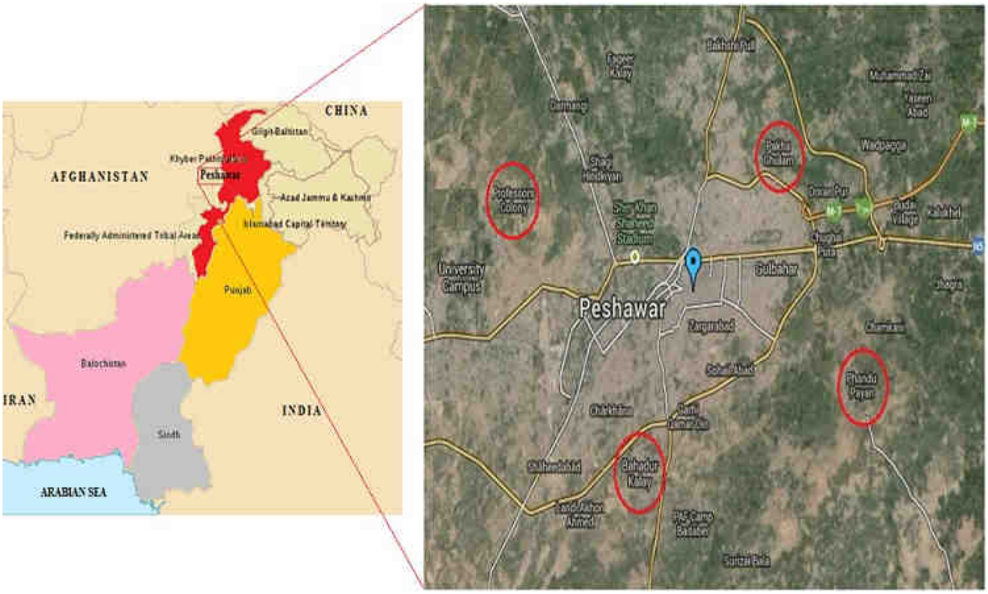

Fig. 1. Location map of the study area and sampling sites

Statistical analysis

Data were statistically analyzed by using SPSS 12 (SPSS Inc., Chicago, IL, USA) software. The concentrations of heavy metals in response to different irrigation systems were tested by analysis of variance (ANOVA; $p = 0.05$) and presented in terms of mean and standard deviation. Least significant difference (LSD) test was used to see the significant difference among the observed means at 5% level of significance.

Results and discussions

Like other under develop countries Pakistan also has poor environmental management. Sewage and industrial wastewater are commonly used as irrigation water for the production of vegetables and other crops particularly in the suburban areas. In the present study, concentration of metals in soil and water used for irrigation were evaluated and the results are summarized in Table 2. The wastewater and wastewater irrigated soils from different localities of Peshawar region shows elevated level of all the metals when compared with tube well water and tube well irrigated soil. Metal contamination in wastewater irrigated soil was in the order of Mn > Fe > Zn and Pb with mean concentration 5.12, 3.8, 2.10, and 0.92 mg · kg^{-1} respectively, while tube well irrigated soil contained higher level of Fe followed by Mn and Zn with mean concentration 3.10, 1.63 and 1.29 mg · kg^{-1} respectively. The higher metal concentration was observed for Fe, Zn and Pb in wastewater samples whereas, the concentration of these elements was quite low in tube well water while the concentration of Ni and Cr was not detected.

Metals accumulation in vegetables

Vegetables are important part of human diet and play a vital role in the human nutrition since the beginning of human life. However, the edible portion of vegetables varies and depends upon the tradition and specific vegetables to be consumed such as leaves for spinach and root for radish etc. The concentrations of heavy metals in the edible portion of vegetables are shown in Figure 2. It is evident from the data that heavy metal concentration in the edible part of vegetables irrigated with waste water was significantly higher ($p < 0.05$), as compared to tube well irrigated vegetables. The selected metals maintained the order of Fe > Mn > Pb > Ni > Zn > Cd > Cr > Co for both the waste water and tube well water irrigated vegetables. The Fe concentrations were in the range of 4.2 to 16.25 mg · kg^{-1} and 2.85 to 11.7 mg · kg^{-1} for wastewater and tube water irrigated vegetables respectively, which shows a significant difference between the two irrigation systems for heavy metal uptake by plants (Tables 3 and 4). Spinach accumulated the highest level of Fe in the range of 8.62-16.25 mg · kg^{-1} among all the vegetables showing significant increase ($p < 0.05$), with wastewater irrigation. Radish irrigated with wastewater also accumulated significantly elevated level ($p < 0.01$) of Fe than tube well water irrigated. The Fe content in various vegetables showed the order of, spinach > lettuce > radish > cabbage with significant high ($p < 0.01$) accumulation having wastewater irrigation source. Iron is relatively abundant in the earth crust and is considered being an important element for plant and human. It was reported previously that plant leaves are the major sink for Fe accumulation where it is used to build chlorophyll content [29]. Iron becomes toxic to plants when its accumulation exceeds 300 mg · kg^{-1} especially at the soil having pH less than 5.0 [8].

Table 2

Heavy metal concentration in irrigation water and soil of the study area [mg kg^{-1}]

Metals	Tube well water	Wastewater	Tube well water irrigated soil	Wastewater irrigated soil
Ni	bdl	0.052	0.099	0.58
Cr	bdl	0.07	0.162	0.42
Cd	0.013	0.054	0.072	0.12
Pb	0.062	0.21	0.351	0.92
Zn	0.087	0.41	1.29	2.1
Fe	0.926	2.31	3.101	3.8
Mn	0.038	0.182	1.632	5.13
Co	0.019	0.152	0.144	0.16

The results clearly depicted the same trend for all other metals *ie*, higher accumulation in wastewater irrigated vegetables and low in tube well irrigated vegetables. The level of Mn were in the range of 2.64 to 7.5 and 1.0 to 4.87 mg · kg^{-1} for wastewater and tube well irrigated vegetables respectively (Tables 3, 4). Comparing the level of Mn in edible part of vegetable, radish contained the highest level while cauliflower with the lowest level (Fig. 2). It was found that Mn concentration was significantly higher in wastewater irrigated vegetables than tube well irrigated. Manganese levels estimated in the present study are much higher than the safe limit of 0.2 mg kg^{-1} according to WHO/EU [30], but are consistent with that of Farooq et al [31]. Sridhara Chary, Kamala, and Raj [32] reported the accumulation of Mn in A. cepa to a level of 5.39 mg · kg^{-1}. The factors responsible for the high content of Mn in vegetables were proposed to be the soil type and the application of agricultural inputs such as pesticides and fertilizer [32]. The concentration of Pb in wastewater and tube well water irrigated vegetables was in the range of 0.65 to 3.12 and 0.09 to 1.83 mg · kg^{-1} respectively (Tables 3, 4).

Table 3

Heavy metal concentration in wastewater irrigated plants on dry weight basis [mg · kg^{-1}]

Metals	Values	Radish	Cabbage	Lettuce	Cauliflower	Spinach
Ni	Range	0.98-1.64	1.25-2.61	1.07-1.84	1.53-2.55	1.82-2.93
	Mean±S.D	1.38±0.04	1.86±0.03	1.43±0.04	1.97±0.06	2.1±0.04
Cr	Range	0.34-0.56	0.20-0.53	0.26-0.54	0.52-0.91	0.24-0.62
	Mean±S.D	0.47±0.02	0.38±0.02	0.41±0.03	0.68±0.04	0.51±0.03
Cd	Range	0.17-0.62	0.08-0.34	0.39-0.72	0.21-0.44	0.27-0.85
	Mean±S.D	0.33±0.01	0.26±0.01	0.51±0.02	0.37±0.01	0.62±0.03
Pb	Range	1.89-3.12	1.73-2.83	0.86-1.88	0.65-1.62	1.27-2.60
	Mean±S.D	2.91±0.04	2.24±0.04	1.52±0.03	1.32±0.02	1.84±0.03
Zn	Range	0.99-1.92	0.38-2.21	0.41-0.92	0.39-0.68	0.28-0.73
	Mean±S.D	1.62±0.02	1.38±0.03	0.84±0.02	0.59±0.05	0.63±0.03
Fe	Range	11.31-14.3	11.56-13.57	12.1-15.1	4.2-8.45	8.62-16.25
	Mean±S.D	12.21±0.05	12.84±0.06	13.2±0.04	7.43±0.04	13.8±0.06
Mn	Range	6.92-7.54	3.86-5.23	2.6 4-4.12	1.78-3.21	3.73-4.86
	Mean±S.D	7.32±0.03	4.93±0.04	3.65±0.05	2.82±0.03	4.62±0.05
Co	Range	0.31-0.75	0.36-0.42	0.27-0.74	0.17-0.31	0.49-0.76
	Mean±S.D	0.66±0.02	0.37±0.01	0.48±0.03	0.29±0.02	0.54±0.02

Table 4

Heavy metal content in tube well water irrigated plants on dry weight basis [mg · kg^{-1}]

Metals	Values	Radish	Cabbage	Lettuce	Cauliflower	Spinach
Ni	Range	0.08-0.76	0.86-1.22	0.25-0.84	0.46-1.2	0.09-0.81
	Mean±S.D	0.52±0.06	0.94±0.03	0.57±0.02	0.78±0.04	0.41±0.03
Cr	Range	0.17-0.302	0.10-0.205	0.13-0.241	0.26-0.41	0.12-0.29
	Mean±S.D	0.21±0.03	0.16±0.04	0.19±0.02	0.34±0.03	0.21±0.02
Cd	Range	0.1-0.42	0.04-0.12	0.16-0.27	0.12-0.38	0.04-0.32
	Mean±S.D	0.27±0.02	0.09±0.02	0.22±0.03	0.24±0.03	0.19±0.02
Pb	Range	0.33-1.59	0.09-1.83	0.74-2.2	0.10-0.46	0.92-1.32
	Mean±S.D	1.15±0.04	0.97±0.02	1.52±0.05	0.26±0.01	1.2±0.04
Zn	Range	0.52-1.48	0.05-0.06	0.22-0.51	0.09-0.28	0.09-0.56
	Mean±S.D	0.96±0.03	0.04±0.01	0.38±0.04	0.15±0.01	0.31±0.02
Fe	Range	2.85-6.73	4.20-9.41	3.10-9.4	2.59-5.43	3.95-11.7
	Mean±S.D	4.63±0.05	7.1±0.06	6.8±0.05	4.2±0.05	8.61±0.05
Mn	Range	3.42-4.873	1.94-3.62	1.22-2.21	0.88-1.76	1.0-3.02
	Mean±S.D	2.26±0.04	2.93±0.03	1.75±0.06	1.4±0.04	1.92±0.04
Co	Range	0.27-0.416	0.19-0.28	0.22-0.46	0.09-0.162	0.20-0.81
	Mean±S.D	0.33±0.03	0.24±0.01	0.29±0.03	0.13±0.02	0.42±0.01

Among the edible parts, Pb was found maximum in radish (Fig. 2). Levels of Pb in the studied vegetables exceeded the safe limit of 0.3 mg/kg recommended by FAO/WHO [33]. One of the explanations for higher level of Pb in wastewater and some tube well irrigated vegetables could be the uptake of Pb promoted by soil pH and the levels of organic matter.

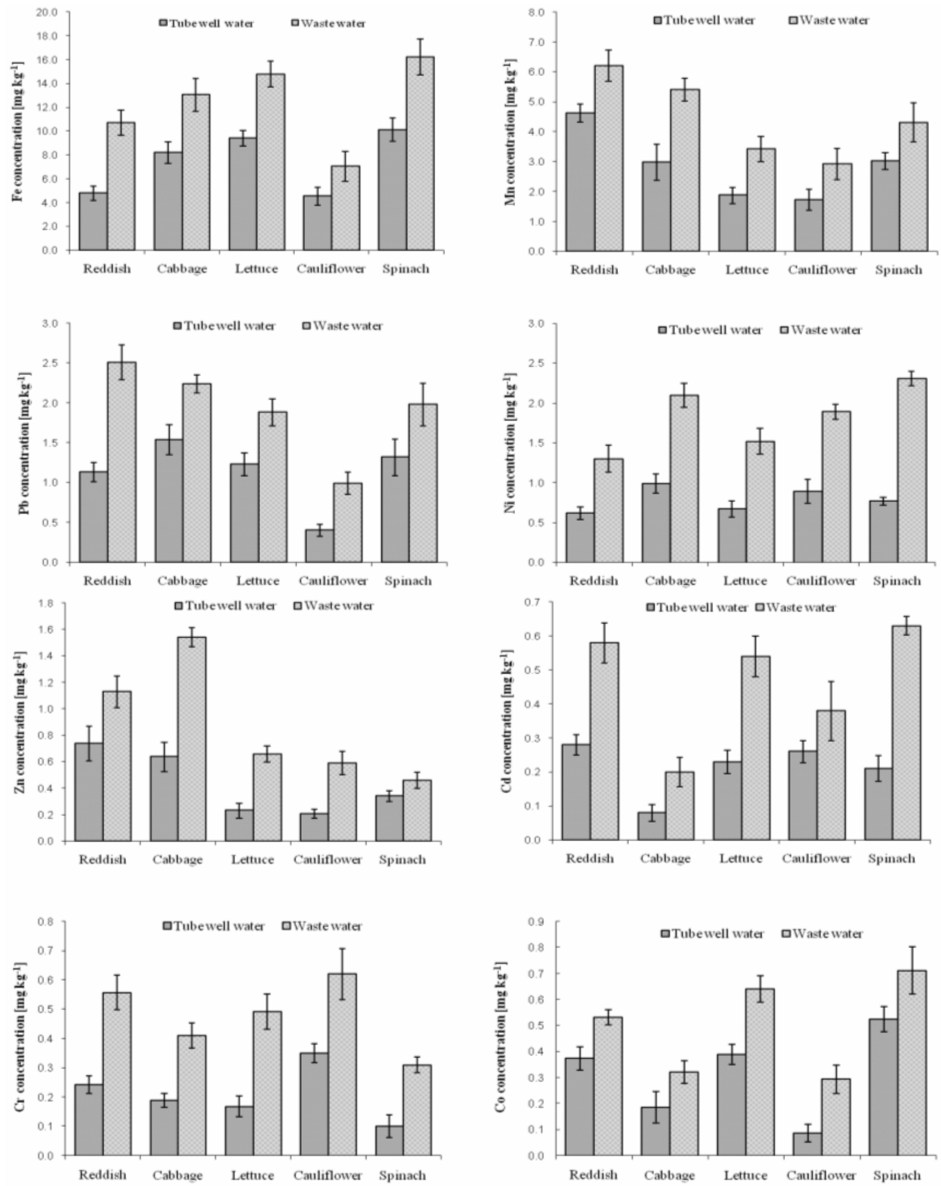

Fig. 2. Heavy metal concentration in edible parts of commonly consumed vegetables irrigated with wastewater and tube well water of the studied area

The high level of lead in waste water irrigated vegetables could be attributed to acid-lead batteries, household and industrial wastes discharged in the irrigation system. In a previous study Demirezen and Ahmet [34] reported a high concentration (3.0 to 10.7 $mg \cdot kg^{-1}$) of Pb which poses health risks to human life. In another study Al Jassir et al [35] studied 6 washed and unwashed green leafy vegetables from Saudi Arabia and observed the concentration of Pb in the coriander (0.171 mg · kg^{-1}) and purslane (0.226 mg · kg^{-1}). Several pathological conditions are associated with Pb intoxication in children and adults such as nervous and immune systems disorder, anemia and reduced hemoglobin synthesis, cardiovascular diseases and bone metabolism, and also renal and reproductive dysfunction [36, 37]. Nickel was found in the range of 0.98 to 2.93 mg · kg^{-1} and 0.08 to 2.61 mg · kg^{-1} in wastewater and tube well irrigated vegetables of the studied area respectively. Maximum accumulation of Ni was observed in edible part of spinach (Fig. 2). The data for Ni showed highly significant difference (p < 0.01) between wastewater and tube well water irrigated vegetables. The concentration of Ni in wastewater irrigated vegetable were in the range of 0.98 to 2.93 mg · kg^{-1} which are in good agreement with 0.99 mg · kg^{-1} reported by Jan et al [7] and 1.20 mg · kg^{-1} reported by Pasha et al [38]. However the results of this study exceeded the permissible limit 0.2 mg · kg^{-1} by WHO/EU [30]. The primary source of Ni is ultramafic rocks and the soil derived from these rocks. However it is also used extensively as catalyst in different industrial and chemical processes [39]. The concentration of Zn in all vegetable was in the range of 0.28 to 2.21 mg · kg^{-1} for wastewater and 0.07 to 0.86 mg · kg^{-1} for tube well irrigated (Tables 3, 4). The maximum accumulation of Zn was found in edible part of cabbage exposed to wastewater irrigation source which shows highly significant difference (p < 0.01), from tube well irrigated source (Fig. 2). The edible part of spinach accumulated the minimum level of Zn, having no significant difference between two sources of irrigation.

Cadmium was highly accumulated by radish, lettuce and spinach irrigated with wastewater showing highly significant difference (p < 0.01) for wastewater and tube well water irrigation. Among all of the heavy metals Zn is considered to be the least toxic and essential element for human beings as it is needed to maintain normal function of body immune system. Intake of too much Zn in the diet is less detrimental than its deficiency. However, it was also reported that high concentration of Zn in vegetables can cause vomiting, renal damage and cramps [40]. The concentration of Zn in vegetables determined by Zakir et al [41] is much higher than the present value while the concentration of Zn in the same vegetables recorded by Bo et al [42] is in good agreement to the present study. The value of Zinc in wastewater irrigated vegetables was found higher than the safe limits 0.3 and 0.2 mg · kg^{-1} [30, 33]. The range of cadmium for wastewater and tube well water irrigated vegetables were 0.08 to 0.85 and 0.04 to 0.38 mg · kg^{-1} respectively (Tables 3, 4). Our results for Cd in wastewater and tube well irrigated vegetables showed higher levels than 0.01 mg · kg^{-1}, a safe limit set by WHO [30]. Demirezen and Ahmet [34] reported Cd content (0.24-0.97 mg · kg^{-1}) in various vegetables and suggested unsuitable for human consumption. Chromium was also found in elevated level in all the studied vegetables irrigated with wastewater. The maximum accumulation of Cr was observed in edible part of cauliflower followed by radish irrigated with wastewater (Fig. 2). The overall range of Cr was 0.20 to 0.91 mg · kg^{-1} and 0.10 to 0.41 mg · kg^{-1} for wastewater and tube well water as irrigation source respectively (Tables 2, 3). Accumulation of Cr in the studied vegetables was lowest in waste water irrigated vegetables compared to the rest of the metals except cobalt. These results are consistent with previous studies which reported that Cr is least accumulated in cabbage [43, 44]. However, the Cr level exceeded the safe limit 0.1 mg · kg^{-1} set by WHO/EU [30]. The high content of Cr in wastewater irrigated vegetables may be attributed to the discharge of Cr based effluent from tanneries in the river and downstream in the irrigation system.

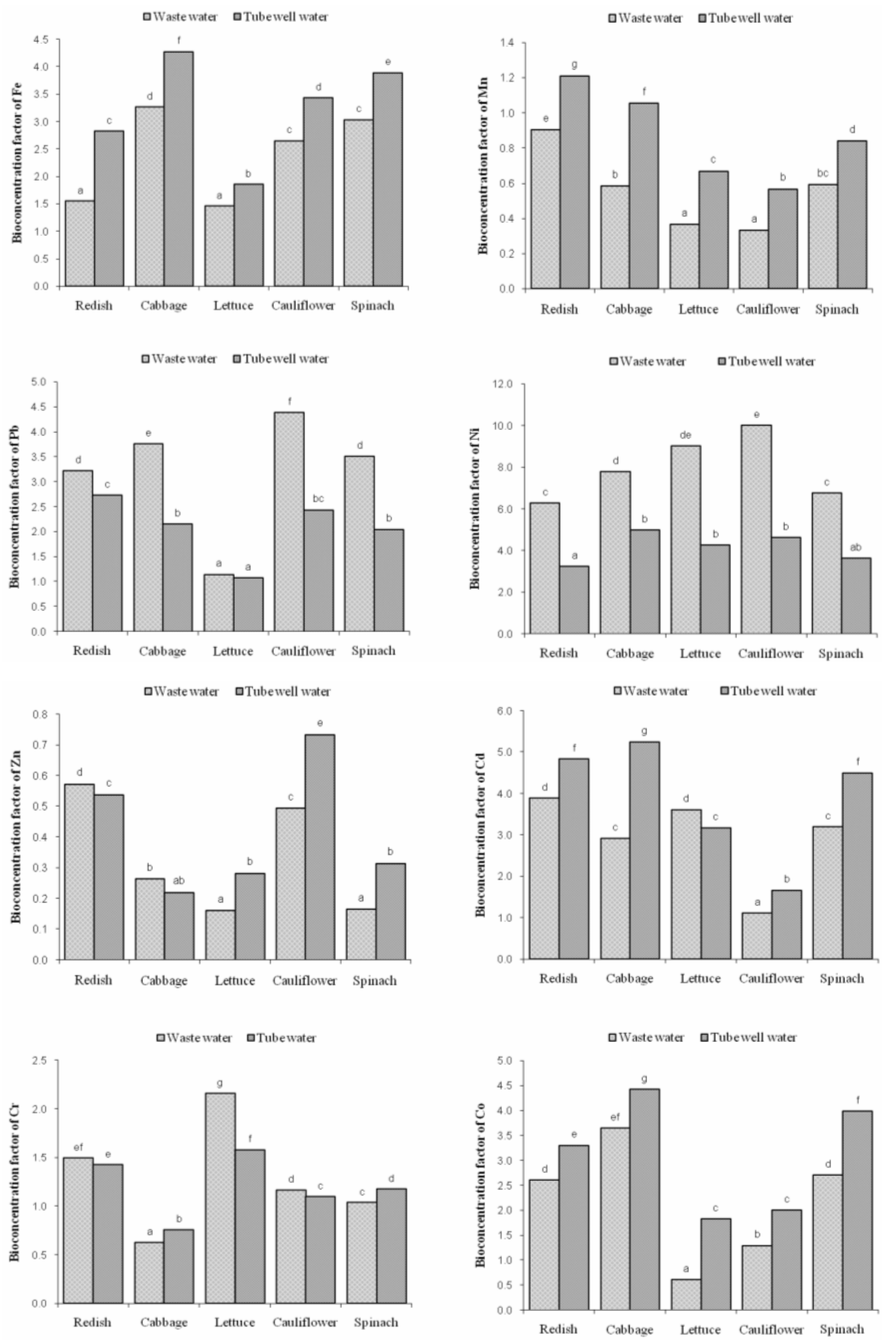

Fig. 3. Bio-concentration factor of different heavy metals in vegetables irrigated with wastewater and tube well water of the studied area. Bars labeled with different letters indicate significant differences among means determined by using least significant difference test ($p > 0.05$)

Accumulation of Co was significantly higher in waste water irrigated vegetables in the same way as in the case of other metals. Among all the vegetables spinach was observed to accumulate higher amount of Co irrespective of the irrigation source (0.49 to 0.76 mg · kg^{-1}), while the concentration of Co was in the range of 0.17 to 0.76 mg · kg^{-1} and 0.09 to 0.81 mg · kg^{-1} for all the vegetables in wastewater and tube well water irrigation system respectively (Tables 2, 3). Cobalt has been known for biochemical functions and was detected in legumes, spinach, cabbage, lettuce, beet greens and figs while higher plants may not require this metal [26, 44, 45]. In our study the Co concentration was higher than 0.01 to 1.0 mg · kg^{-1} reported by Khan et al [16]. However, the concentrations were found consistent with the normal range in edible parts of vegetables.

Bioconcentration factor (BCF)

Bioconcentration factor was determined in the selected vegetables for the studied metals. The results are given in the form of figures. Generally the BCF values were higher for tube well irrigated vegetables as compared to waste water irrigated vegetables. Nickel accumulation was significantly higher ($p < 0.05$), in cauliflower and lettuce when irrigated with tube well water. The highest BCF value for Cd was observed in cabbage when irrigated with tube well water, showing significant difference from the rest of vegetables. Maximum BCF value of lead was calculated for cauliflower when irrigated with wastewater (Fig. 3). It was also observed that all the BCF values for Pb in wastewater irrigated was found significantly greater ($p < 0.05$), than tube well water irrigated vegetables except lettuce. Cabbage showed the highest BCF value for Co having tube well water as irrigation source. In case of Cr, Fe and Zn the maximum BCF value was recorded in lettuce, cabbage and cauliflower respectively when irrigated with tube well water, while the greatest BCF value for Mn was observed in radish having tube well water as irrigation source. The overall trend of BCF values for the metals in selected vegetables were Pb > Cd > Ni > Cr > Co > Fe > Mn > Zn and Ni > Cd > Pb > Fe > Co > Cr > Mn > Zn, for wastewater and tube well water respectively (Fig. 3).

Daily intake of metal

Human exposure to hazardous material can occur through various means, among these, food chain transfer is the most important one. In the present study daily intake of the selected metals in various vegetables consumed in the target areas were estimated for both children and adults on daily basis. The daily intake of metal (DIM) through the five commonly consumed vegetables is given in Tables 5 and 6. The data showed that the DIM for all the metals through the consumption of vegetable irrigated with wastewater was higher in both adults and children when compared with tube well irrigated vegetables. In case of children the DIM in wastewater irrigated vegetables was found to be highest for Fe ($9.80 \cdot 10^{-3}$) followed by Mn ($3.74 \cdot 10^{-3}$), Pb ($1.51 \cdot 10^{-3}$), Ni ($1.39 \cdot 10^{-3}$), Zn ($9.29 \cdot 10^{-4}$), Cd ($3.80 \cdot 10^{-4}$), Cr ($3.74 \cdot 10^{-4}$) and Co ($4.29 \cdot 10^{-4}$), while in tube well irrigated vegetables the order was Fe ($6.10 \cdot 10^{-3}$), Mn ($2.79 \cdot 10^{-3}$), Pb ($9.29 \cdot 10^{-4}$), Ni ($5.97 \cdot 10^{-4}$), Zn ($4.45 \cdot 10^{-4}$), Co ($3.17 \cdot 10^{-4}$), Cr ($2.11 \cdot 10^{-4}$), and Cd ($1.69 \cdot 10^{-4}$). Daily intake of metal for adults showed the order of Fe ($6.53 \cdot 10^{-3}$), Mn ($2.49 \cdot 10^{-3}$), Ni ($9.28 \cdot 10^{-4}$), Pb ($9.00 \cdot 10^{-4}$), Zn ($6.19 \cdot 10^{-4}$), Co ($2.86 \cdot 10^{-4}$), Cd ($2.53 \cdot 10^{-4}$) and Cr ($2.49 \cdot 10^{-4}$) in wastewater irrigated vegetables, where in tube well water irrigated vegetables the DIM for adults was in the following manner Fe ($4.07 \cdot 10^{-3}$), Mn ($1.86 \cdot 10^{-3}$), Ni ($3.98 \cdot 10^{-4}$), Pb ($6.19 \cdot 10^{-4}$), Zn ($2.96 \cdot 10^{-4}$), Co ($2.11 \cdot 10^{-4}$), Cd ($1.12\cdot10^{-4}$) and Cr ($1.41\cdot10^{-4}$). Daily intake of metal was also observed to be more dependent on the species of vegetable, the trend for maximum DIM was in order of spinach > radish > cauliflower > lettuce > and cabbage. To understand the phenomena of risk pertaining to any chemical pollutant, it is imperative to notice the exposure concentration by measuring the route of exposure of the pollutant to the target organism. Food chain exposure is considered to be one of the most important pathways for exposure to many pollutants including heavy metals. In the present study vegetables grown on wastewater irrigated soils may cause health risk for the local population due to metal contamination. It is evident from the present data that estimated DIM for children and adults through consumption of vegetables irrigated with wastewater is higher than vegetables grown on tube well water, but the consumption of these vegetable is risk free as the oral reference dose for Zn, Cd, Pb, Ni, Cr and Mn are $3.0\cdot10^{-1}$, $1.0\cdot10^{-1}$, $4.0\cdot10^{-3}$, $2.0\cdot10^{-2}$, 1.5, and $3.3\cdot10^{-2}$ mg · kg^{-1}/day, respectively [7]. However, it represents only one route for metals exposure, there are many other sources such as skin contact, inhalation of dust, and ingestion of metal-polluted soils, which may increase the cumulative risk of metal but not dealt with in the present study.

Table 5

Daily intake of metal (DIM) due to consumption of wastewater irrigated vegetables in the study area [mg · kg^{-1}]

Metal	Adults					Children				
	Radish	**Cabbage**	**Lettuce**	**Cauli-flower**	**Spinach**	**Reddish**	**Cabbage**	**Lettuce**	**Cauli-flower**	**Spinach**
Ni	$5.22\cdot10^{-4}$	$8.44\cdot10^{-4}$	$6.11\cdot10^{-5}$	$7.59\cdot10^{-4}$	$9.28\cdot10^{-4}$	$7.84\cdot10^{-4}$	$1.27\cdot10^{-3}$	$9.17\cdot10^{-4}$	$1.14\cdot10^{-3}$	$1.39\cdot10^{-3}$
Cr	$2.24\cdot10^{-4}$	$1.65\cdot10^{-4}$	$1.98\cdot10^{-4}$	$2.49\cdot10^{-4}$	$1.25\cdot10^{-4}$	$3.36\cdot10^{-4}$	$2.48\cdot10^{-4}$	$2.97\cdot10^{-4}$	$3.74\cdot10^{-4}$	$1.87\cdot10^{-4}$
Cd	$2.33\cdot10^{-4}$	$8.03\cdot10^{-5}$	$2.17\cdot10^{-4}$	$1.53\cdot10^{-4}$	$2.53\cdot10^{-4}$	$3.50\cdot10^{-4}$	$1.21\cdot10^{-4}$	$3.26\cdot10^{-4}$	$2.30\cdot10^{-4}$	$3.80\cdot10^{-4}$
Pb	$1.01\cdot10^{-3}$	$9.00\cdot10^{-4}$	$7.56\cdot10^{-4}$	$3.98\cdot10^{-4}$	$7.95\cdot10^{-4}$	$1.51\cdot10^{-3}$	$1.35\cdot10^{-3}$	$1.13\cdot10^{-3}$	$5.97\cdot10^{-4}$	$1.19\cdot10^{-3}$
Zn	$4.54\cdot10^{-4}$	$6.19\cdot10^{-4}$	$2.65\cdot10^{-4}$	$2.37\cdot10^{-4}$	$1.85\cdot10^{-4}$	$6.81\cdot10^{-4}$	$9.29\cdot10^{-4}$	$3.97\cdot10^{-4}$	$3.56\cdot10^{-4}$	$2.77\cdot10^{-4}$
Fe	$4.31\cdot10^{-3}$	$5.24\cdot10^{-3}$	$5.95\cdot10^{-3}$	$2.83\cdot10^{-3}$	$6.53\cdot10^{-3}$	$6.47\cdot10^{-3}$	$7.87\cdot10^{-3}$	$8.93\cdot10^{-3}$	$4.25\cdot10^{-3}$	$9.80\cdot10^{-3}$
Mn	$2.49\cdot10^{-3}$	$2.17\cdot10^{-3}$	$1.37\cdot10^{-3}$	$1.16\cdot10^{-3}$	$1.73\cdot10^{-3}$	$3.74\cdot10^{-3}$	$3.26\cdot10^{-3}$	$2.06\cdot10^{-3}$	$1.75\cdot10^{-3}$	$2.59\cdot10^{-3}$
Co	$2.13\cdot10^{-4}$	$1.29\cdot10^{-4}$	$2.57\cdot10^{-4}$	$1.18\cdot10^{-4}$	$2.86\cdot10^{-4}$	$3.20\cdot10^{-4}$	$1.94\cdot10^{-4}$	$3.87\cdot10^{-4}$	$1.77\cdot10^{-4}$	$4.29\cdot10^{-4}$

Table 6

Daily intake of metal (DIM) due to consumption of tube well water irrigated vegetables in the study area [mg · kg^{-1}]

Metal	Adults					Children				
	Radish	**Cabbage**	**Lettuce**	**Cauli-flower**	**Spinach**	**Reddish**	**Cabbage**	**Lettuce**	**Cauli-flower**	**Spinach**
Ni	$2.49\cdot10^{-4}$	$3.98\cdot10^{-4}$	$2.69\cdot10^{-4}$	$3.59\cdot10^{-4}$	$3.09\cdot10^{-4}$	$3.74\cdot10^{-4}$	$5.97\cdot10^{-4}$	$4.04\cdot10^{-5}$	$5.39\cdot10^{-4}$	$4.64\cdot10^{-4}$
Cr	$9.72\cdot10^{-5}$	$7.59\cdot10^{-5}$	$6.75\cdot10^{-5}$	$1.41\cdot10^{-4}$	$4.06\cdot10^{-5}$	$1.46\cdot10^{-4}$	$1.14\cdot10^{-4}$	$1.01\cdot10^{-5}$	$2.11\cdot10^{-4}$	$6.09\cdot10^{-5}$
Cd	$1.12\cdot10^{-4}$	$3.21\cdot10^{-5}$	$9.24\cdot10^{-5}$	$1.04\cdot10^{-4}$	$8.44\cdot10^{-5}$	$1.69\cdot10^{-4}$	$4.82\cdot10^{-5}$	$1.39\cdot10^{-5}$	$1.57\cdot10^{-4}$	$1.27\cdot10^{-4}$
Pb	$4.54\cdot10^{-4}$	$6.19\cdot10^{-4}$	$4.94\cdot10^{-4}$	$1.61\cdot10^{-4}$	$5.30\cdot10^{-4}$	$6.81\cdot10^{-4}$	$9.29\cdot10^{-4}$	$7.42\cdot10^{-5}$	$2.41\cdot10^{-4}$	$7.96\cdot10^{-4}$
Zn	$2.96\cdot10^{-4}$	$2.56\cdot10^{-4}$	$8.56\cdot10^{-5}$	$8.32\cdot10^{-5}$	$1.37\cdot10^{-4}$	$4.45\cdot10^{-4}$	$3.84\cdot10^{-4}$	$1.28\cdot10^{-5}$	$1.25\cdot10^{-4}$	$2.05\cdot10^{-4}$
Fe	$1.93\cdot10^{-3}$	$3.30\cdot10^{-3}$	$3.78\cdot10^{-3}$	$1.82\cdot10^{-3}$	$4.07\cdot10^{-3}$	$2.89\cdot10^{-3}$	$4.95\cdot10^{-3}$	$5.67\cdot10^{-3}$	$2.73\cdot10^{-3}$	$6.10\cdot10^{-3}$
Mn	$1.86\cdot10^{-3}$	$1.20\cdot10^{-3}$	$7.50\cdot10^{-4}$	$6.83\cdot10^{-4}$	$1.21\cdot10^{-3}$	$2.79\cdot10^{-3}$	$1.80\cdot10^{-3}$	$1.13\cdot10^{-3}$	$1.03\cdot10^{-3}$	$1.82\cdot10^{-3}$
Co	$1.50\cdot10^{-4}$	$7.47\cdot10^{-5}$	$1.56\cdot10^{-4}$	$3.49\cdot10^{-5}$	$2.11\cdot10^{-4}$	$2.26\cdot10^{-4}$	$1.12\cdot10^{-4}$	$2.35\cdot10^{-4}$	$5.25\cdot10^{-5}$	$3.17\cdot10^{-4}$

Conclusions

Analysis of five vegetables grown on wastewater irrigated soils revealed excessive buildup of heavy metals. Accumulation of Mn, Pb, Ni, Zn, Cr and Cd were significantly ($p < 0.05$, $p < 0.01$) above for wastewater irrigated vegetables, which exceeded the permissible limits of WHO/EU [30]. The estimated DIM indicated that residents of Peshawar city are exposed to heavy metals through consumption of contaminated vegetables. However, at present the consumption of these vegetables is risk free but the situation can be hazardous in future if proper environmental control measures would not be adopted. It is also recommended that industrial effluents and wastewater must be treated before their discharge to irrigation system.

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POBIERANIE METALI PRZEZ WARZYWA NAWADNIANE ŚCIEKAMI I ICH DZIENNE STĘŻENIE W DIECIE LUDNOŚCI PESZAWARU, PAKISTAN

Abstrakt: Warzywa są ważnym źródłem składników odżywczych dla organizmu człowieka. Nawadnianie ściekami może prowadzić do zanieczyszczenia tych warzyw i powodować zagrożenie dla zdrowia. Zbadano wpływ nawadniania roślin ściekami na pobieranie metali (Fe, Mn, Ni, Co, Zn, Cd, Cr i Pb) przez pięć powszechnie spożywanych warzyw (rzodkiewka, kapusta, sałata, kalafior i szpinak), uprawianych na przedmieściach Peszawaru. Stężenia metali oznaczono za pomocą AAS (atomowej spektrometrii absorpcyjnej). Pobieranie i akumulacja metali w warzywach nawadnianych ściekami były istotnie ($p < 0,05$) wyższe niż dopuszczalne granice podawane przez WHO/FAO. Wśród części jadalnych warzyw maksymalna akumulacja Mn, Pb i Cd wystąpiła w rzodkiewce, Ni i Fe w szpinaku, natomiast Cr i Zn w kalafiorze i kapuście. Oszacowane dzienne stężenie metali w diecie ludności wykazało, że obecna ich ilość w badanych warzywach mieściła się w dopuszczalnych granicach (US-EPA, IRIS), jednak stężenia metali w warzywach nawadnianych ściekami były wysokie, co może powodować zagrożenie dla zdrowia w dłuższym okresie.

Słowa kluczowe: metale ciężkie, warzywa, dzienne stężenie metali w diecie ludności, ścieki, czynnik biokoncentracji, Peszawar