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Risk Assessment of Trace and Toxic Elements (Cu, Cd, Cr, and As) in Vegetables from District Ghotki, Sindh, Pakistan

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Abstract
This study assessed the concentrations of trace and toxic elements in vegetables using an atomic absorption spectrophotometer by evaluating the Estimated Daily Exposure of Metals (EDEM), Target Hazard Quotient (THQ), and Bio-concentration Factor (BCF). The results showed that copper (Cu) concentrations exceeded the WHO/FAO permissible limit (5 mg/kg) in potato (6.55 mg/kg) and tomato (6.54 mg/kg). In addition, the maximum concentrations of cadmium (Cd) in carrot (0.36 mg/kg), chromium (Cr) in onion (0.21 mg/kg), and arsenic (As) in round melon (0.06 mg/kg) remained within the WHO/FAO permissible limits of 0.6, 0.3, and 0.1 mg/kg, respectively. The Estimated Daily Exposure of Metals (EDEM) for Cr, Cd, Cu, and As was below 1 (mg/kg bw/d), indicating negligible non-carcinogenic health risks to the local population. In general, EDEM or THQ values ≤1 suggest no significant health risk to consumers, whereas values >1 indicate a potential health concern. The EDEM values followed the ascending order: As < Cd < Cr < Cu, whereas the soil-to-plant bio-concentration factors followed the reverse trend: Cu > Cr > Cd > As. Similarly, the Target Hazard Quotient (THQ) values were all below 1 (THQ < 1), with the relative contribution decreasing in the order: Cd > Cr > Cu > As. In conclusion, the findings indicate that consumption of the investigated vegetables does not pose an immediate systemic health risk to local consumers. However, continuous monitoring of trace and toxic metal concentrations, together with proactive regulatory measures, is recommended to minimize long-term accumulation and ensure food safety.

Keywords: Risk assessment, Toxic elements, atomic absorption spectrophotometer, Vegetables

1. Introduction
Vegetables contain minerals, carbohydrates, vitamins, and fiber, which are very important for human beings. Vegetables are light, inexpensive foods and an important part of human life. They are low in calories, sodium, fat, and cholesterol, and are high in fiber. Eating carrots daily helps keep your skin healthy and improves your eyesight [1, 2]. About 10,000 varieties of vegetables, including roots, fruits, and leaves, are cultivated and used around the world [3]. In Pakistan, more than 35 different varieties of vegetables are grown across the country [4] (Fruits, vegetables, condiments statistics of Pakistan). Different kinds of vegetables contain edible roots, stems, leaves, fruits, or seeds [5,6].

Vegetable consumption is considered one of the main pathways for dietary exposure to heavy metals. When these toxic heavy elements enter, they are placed in bone and fat tissues, overlying the main minerals. Slowly released into the body, heavy metals can cause an array of chronic problems like cancer, liver diseases, etc. [7, 8]. Several epidemiologic surveys have recognized that chronic exposure to toxic elements such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Mercury (Hg), Selenium (Se), and Lead (Pb), even at trace levels, is related to many diseases, such as dermal, cardiac, neurological, bone diseases, and cancers [9,10]. Vegetables grown on contaminated land may accumulate trace and toxic elements. Long-term consumption of polluted food may lead to the continuous accumulation of toxic elements in the human liver and kidneys, causing problems such as liver, kidney, cardiovascular, nervous, and bone disorders [11,12].

Air pollution may endanger post-harvest vegetables during transportation and marketing by increasing the levels of toxic elements in the vegetables. Elevated heavy metal levels in vegetables have been reported due to long-term use of treated or untreated wastewater. Other anthropogenic sources of heavy metals include the addition of manures, sewage sludge, fertilizers, and pesticides, which may affect heavy metal uptake by modifying the physicochemical properties of the soil, such as pH, organic matter, and the bioavailability of heavy metals in the soil [13-15].

1.1. Classification of vegetables

1.2. Leaf vegetables
This group contains spinach, coriander leaves, cabbage, etc. These are important minerals (iron and calcium), vitamins (A, C, and riboflavin), and sources of fiber. The green outer leaves of lettuce and cabbage are richer in vitamins, calcium, and iron than the white inner leaves. Thinner, greener leaves are more nutritious and usually have fewer calories.

1.3. Fruit and flower vegetables
Brinjals, ladyfingers, tomatoes, bitter gourds, round melons/squash, and green chilies are fruit vegetables, whereas cauliflowers are included in flower vegetables. Fruits and vegetables contain vitamins, minerals, proteins, and other

nutrients. Cauliflower is also a good source of vitamin C. The nutritional value of the outer leaves of cauliflower and broccoli is much higher than that of the flower buds. They can be consumed raw in salads or cooked.

1.4. Root vegetables

Potatoes, turnips, onions, carrots, and garlic are examples of this group of vegetables. The yellow and orange varieties are rich in β-carotene, a precursor of vitamin A. The onion is an exceptional root vegetable and contains moderate levels of vitamin C [16]. The interactions among the micronutrients and antioxidants found in vegetables have important health impacts. For instance, higher birth weight among children in India was associated with mothers consuming more green leafy vegetables and fruits during pregnancy [17].

The present study aimed to evaluate the concentrations of trace and toxic elements, including copper (Cu), cadmium (Cd), chromium (Cr), arsenic (As), in 15 rooty, leafy, and fruity green edible parts of vegetables like potato, turnip, onion, carrot, garlic, bitter gourd, coriander leaves, cauliflower, cabbage, brinjal, ladyfinger/okra, spinach, round melon/squash, tomato, and green chilies which are grown on the same agricultural soil in respective areas of Sindh, Pakistan.

The objectives of this study were also to evaluate the concentrations of trace and toxic elements and correlate the presence of elemental pollution in fresh green vegetables; determine the Target Hazard Quotient (THQ) of the edible vegetable parts; evaluate the Bio-concentration Factor (BCF) in vegetables; analyze the relationship between the physical and chemical properties of toxic elements in vegetables; estimate the Estimated Daily Exposure (EDEM) of trace elements through the consumption of the selected vegetables; and assess the potential hazardous effects of these contaminants on the health of the local population.

2.0. Materials and Methods

2.1. Study Area

The climatic conditions of Sindh province are divided into two zones, i.e., Northern/Upper Sindh and Southern/Lower Sindh. Northern/Upper Sindh includes famous districts such as Ghotki. The climate of Ghotki is warm in summer, reaching up to 50°C, while in winter it is cold, down to 3°C. The soil of Ghotki is fertile; almost all kinds of cash and cereal crops, as well as vegetables, are cultivated. Ghotki is a district in the Pakistani province of Sindh, with the administrative capital, Mirpur Mathelo. According to the 2023 census, the district had a population of 1772609 in words (seventeen lakh seventy-two thousand six hundred nine only). It covered an area of 6,038 km^2 (six thousand thirty-eight square kilometers).

2.2 Sampling Locations and Collection of the District Ghotki

Five (05) samples of each fresh vegetable were collected separately from each location, including Ghotki, Masoo Khan Kalwar, Adilpur, Jahanpur, and Mirpur Mathelo, by using a random sampling method and transported to the Institute of Chemistry, Shah Abdul Latif University (SALU), Khairpur, for sample preparation. The elemental investigation was performed during this study (Fig. 1).

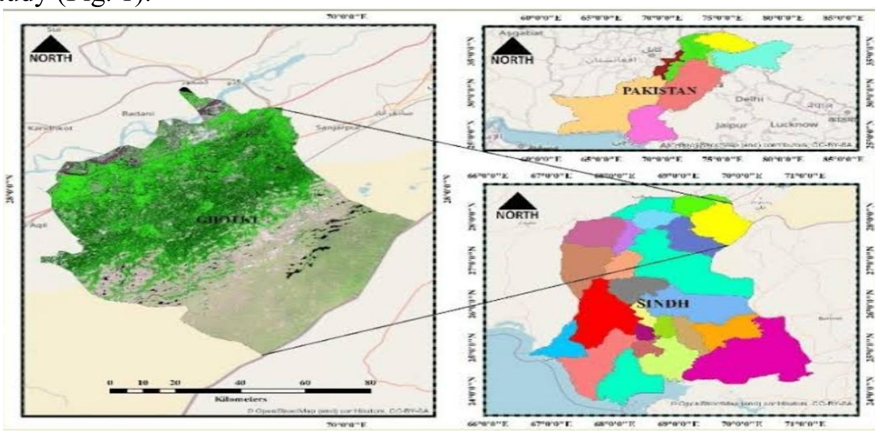

Figure 1. Map of study area

2.3. Procedure of Sampling

One kilogram of fresh vegetables, including onions, carrots, bitter melons, coriander leaves, cauliflowers, turnips, cabbages, brinjals, ladyfingers, garlic, spinach, round melon/squash, potatoes, tomatoes, and green chilies, was taken from various sampling locations throughout the study area. After collecting individual samples from various fields, they were quickly covered with clean aluminum foil and stored in polyethylene plastic bags for further digestion and analysis.

2.4 Preparation of Vegetable Samples

To remove upper contamination from vegetables, first wash with tap water, then with de-ionized water, and then use a stainless-steel cutter to remove the upper layer from all vegetables. After the samples were sliced, they were placed on a 4/4 sheet of full-length plastic paper for approximately two hours to reduce moisture. A digital balance was used to weigh each vegetable sample separately, and the samples were placed in an oven at 80 °C until a constant mass was reached. After obtaining a constant weight, each dry sample was ground using a grinder machine and sieved at 65 mesh. The vegetable samples were then stored in clean, pre-dried glass containers with tight stoppers.

2.5 Digestion of Vegetables

Microwave digestion was used for rapid elemental analysis. For this, a 5 mL volume of 20% HCl and a (1:4) perchloric acid ($HClO_4$) and nitric acid (HNO_3) solution were used. All samples were filtered with Whatman 42. After filtration, deionized water was added to a final volume of 50 mL for accurate analysis of metals such as Cd, Cr, Cu, and As.

2.6. Method of Determination of Heavy Metals by Atomic Absorption Spectrophotometry (AAS)

The concentrations of cadmium (Cd), chromium (Cr), and copper (Cu) were determined using flame atomic absorption spectrophotometry (FAAS using an Atomic Absorption Spectrophotometer (AA-100), whereas arsenic (As) was determined using hydride generation atomic absorption spectrophotometry (HG-AAS) because of its higher analytical sensitivity. The instrument was calibrated using certified multi-element standard solutions, and reagent blanks, together with quality control standards, were analyzed after every 10 samples to verify analytical accuracy. The limits of detection (LOD) and quantification (LOQ) were established from the standard deviation of reagent blanks and the slope of the calibration curves. All samples were analyzed in triplicate, and the results were expressed as mg kg^{-1} on a dry weight basis.

2.7. Estimated Daily Exposure of Metals (EDEM)

Estimated Daily Exposure/Intake of Metals (EDEM)**,** a key metric used in human health risk assessments. The estimated daily intake of metals depends on both the metal concentration in food and the daily food consumption. The EDEM can be calculated by following the formula:

$$EDEM = DIM \div BW$$

EDEM = Estimated daily intake of metals
DIM = Daily intake of metals = daily vegetable consumption x mean metal concentration
BW = Body weight

2.7.1. Targeted Hazard Quotient (THQ)

The targeted hazard quotient is the ratio of exposure to the toxic element to the reference dose, which is the highest level at which no adverse health effects are expected. The THQ describes the non-carcinogenic health risk posed by exposure to the respective toxic element.

$$THQ = (EF \times ED\ FI \times MC \times 10^{-3}) \div (RfD \times BW \times AT)$$

EF = Exposure frequency 365 days/year
ED = Exposure duration 70 years
FI = Food ingestion gram/person/day
MC = Metal concentration in vegetables, mg/kg on a fresh vegetable base
RfD=Oral reference dose mg/kg/day
BW = Body weight 60 kg adult
AT=Average time for non-carcinogen 365 days/year × number of exposure 70 years

2.7.2. Method for Determining Bio-concentration Factor (BCF)

The BCF is calculated as the ratio of the pollutant concentration in the harvested plant to that in the soil. The formula by which BCF can be calculated is according to the following formula,

$$BCF = \frac{C_{\text{organism}}}{C_{\text{water}}}$$

where: C_{organism}= Concentration of the contaminant in the organism (mg/kg dry weight or wet weight)
C_{water}= Concentration of the contaminant in the surrounding water (mg/L)

The unit of BCF is generally L/kg.

2.8. Statistical Analysis

Pearson Correlation was computed using SPSS version 18 installed on Windows 10 (Laptop). This analysis was used to measure the strength and direction of a linear relationship between two continuous variables

3.0. Results and Discussion

5 locations in District Ghotki where vegetables were grown were selected, and from each location, 5 samples of each vegetable were collected in triplicate for analytical investigation of trace and toxic elements. Therefore, a total of 75 vegetable samples are included in this research work. Elements identified in vegetable samples were cadmium (Cd), chromium (Cr), copper (Cu), and arsenic (As), and results are discussed below

3.1.1 Copper (Cu)

Cu in the human body is needed only in trace amounts, such as 100 milligrams, as an important trace element [18]. Beyond its role in iron metabolism, Cu is required for many biological processes, including antioxidant defense, neuropeptide synthesis, and immune function [19]. The results for Cu are shown in Figure 2, indicating maximum concentrations of 6.65 mg/kg in potatoes and 6.54 mg/kg in tomatoes, both exceeding the WHO/FAO limits. The average range of copper was reported (0.21–0.62 mg/kg) in South Korea, which is below that of the present study [20]. The permissible limit of Cu in vegetables is 5mg/kg. Out of 75 samples, only 5 samples of each potato and tomato were above WHO/FAO limits, whereas the remaining samples were within the admissible range set by WHO/FAO.

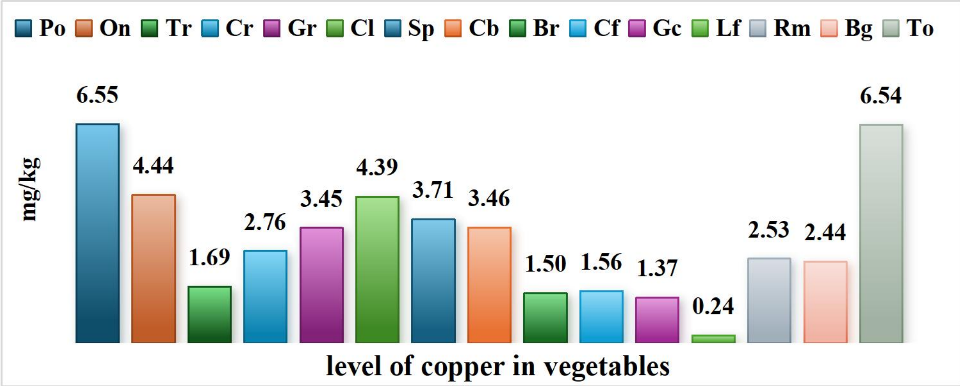

Figure 2. The concentration of Cu in vegetables

3.1.2 Cadmium (Cd)

Cd is a toxic, non-essential element for all living organisms and has no biological function; such elements are very dangerous to human metabolism. Cd is released into the environment through various natural and anthropogenic activities such as mining, smelting, and refining [21]. It is also being used in many other industrial applications, such as plastics, pigments, enamels, ceramics, and steel plating. Cd exposure can occur through water, air, and soil, resulting in Cd toxicity. It mainly accumulates in the roots, shoots, and edible parts of vegetables. Some plants can tolerate a small concentration of it. It enters living beings through crops and vegetables and can cause different chronic diseases like cancer and cardiovascular diseases [22]. Cd accumulation in vegetables is an important environmental issue that threatens human health globally. Understanding how vegetables respond to Cd stress and implementing management strategies may help reduce Cd toxicity. Cadmium toxicity leads to reduced seed germination, growth, and biomass, and decreased vegetable quality. The use of low-seed-accumulation vegetable cultivation, combined with solubilizing modifications and appropriate agricultural practices, can be a useful technique for reducing food-chain risk [23]. Analysis of Cd in leafy vegetables is frequently difficult due to low concentrations and matrix effects (Figure 3) exploits the contents of Cd in the root, fruit, and leaf vegetables. The maximum Cd concentration was found in carrots at 0.36 mg/kg, while the minimum was detected in green chilies and tomatoes at 0.03 mg/kg each. It has been observed that the Cd concentration in all vegetable samples was below 0.6 mg/kg, the safe limit set by WHO/FAO (Fig. 3).

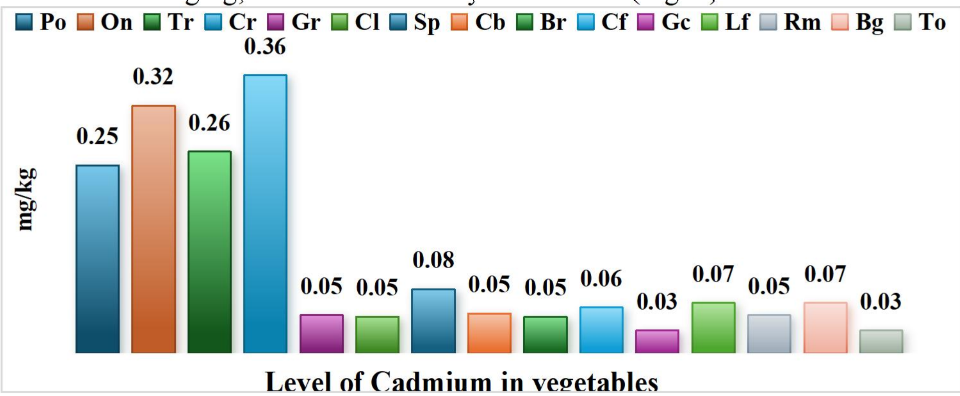

Figure 3. The concentration of Cd in vegetables

3.1.3 Chromium (Cr)

Cr is one of the toxic heavy metals found in various oxidation states in the environment, ranging from +2 to +6, but the most stable forms of Cr are the triplet and hexavalent states. The Cr element, which is abundant in valence state 3, has the weakest absorption in the cell compared to hexavalent Cr^{+6}. The most common routes of exposure to Cr in the human body are ingestion, cutaneous contact, and inhalation in a chromium-polluted environment. The primary health hazards caused by chromium are bronchial asthma, lung problems, and nasal ulcers; risk of cancer, skin allergies, and reproductive disorders[24]. If trivalent chromium is used in excess from any of the sources mentioned above, it can cause sudden death. The concentrations of chromium in the vegetables ranged from 0.063 to 1.05 $mg.kg^{-1}$. The maximum concentration of chromium was 0.21 mg/kg in the onion sample, which exceeds the WHO/FAO limit, and the minimum chromium content was detected in two vegetable varieties, green chili and bitter gourd, at 0.03mg/kg, as shown in Figure 4.

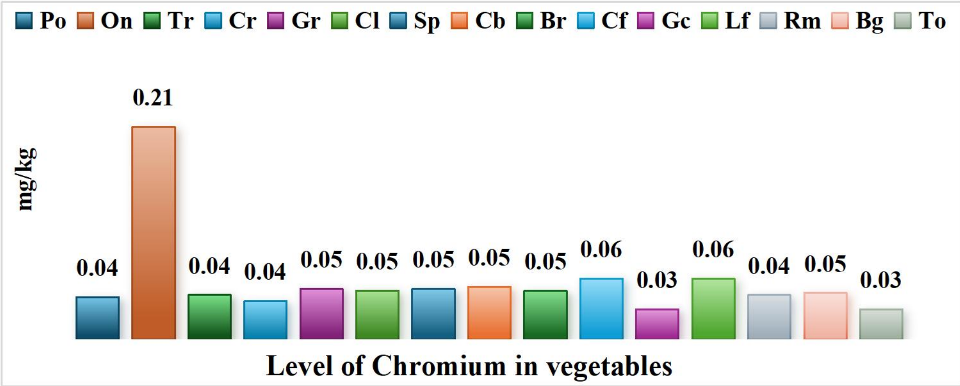

Figure 4. The concentration of Cr in vegetables

3.1.4 Arsenic (As)

Arsenic is a naturally occurring element that is present in the Earth's crust, and there are many sources of arsenic pollution in the environment. It possesses two different valances, +3 and +5. The most dangerous form of Arsenic is As+3, known as inorganic Arsenic, and is highly carcinogenic compared to organic Arsenic, which has a +5-valence state. Arsenic pollution in the environment is now one of the fastest-emerging issues worldwide. These are the various sources of its pollution, which may cause its release in the surrounding areas, including industrial and agricultural pollution. The origin of arsenic pollution is not fully understood, yet it is believed that natural geological weathering is primarily responsible for the arsenic dissolved in groundwater.

Human exposure to arsenic causes degenerative, inflammatory, and neoplastic changes in the skin, respiratory system, blood, lymphatic system, nervous system, and reproductive system [25]. Approximately 100 million people are affected by arsenic diseases now, as reported in the literature worldwide, such as skin spots, high blood pressure, diabetes, bladder, kidney, and lung cancer. There is a strong correlation between chronic ingestion of arsenic and deleterious human health effects. Safe drinking water and nutritious food are essential for preventing chronic arsenic poisoning. Balanced nutritional supplementation may play a major role in preventing chronic arsenic poisoning.

The average concentrations of arsenic in vegetable samples ranged from 0.029 to 0.444 mg/kg [26], which are lower than those reported in the present study. The maximum concentration of arsenic was found in the round melon sample at 0.06 mg/kg, while the concentrations in five different varieties of vegetable onion, carrot, garlic, coriander, and ladyfinger were 0.04mg/kg, respectively (Fig.5). The level of arsenic was found under the WHO/FAO limit of 0.11mg/kg [26].

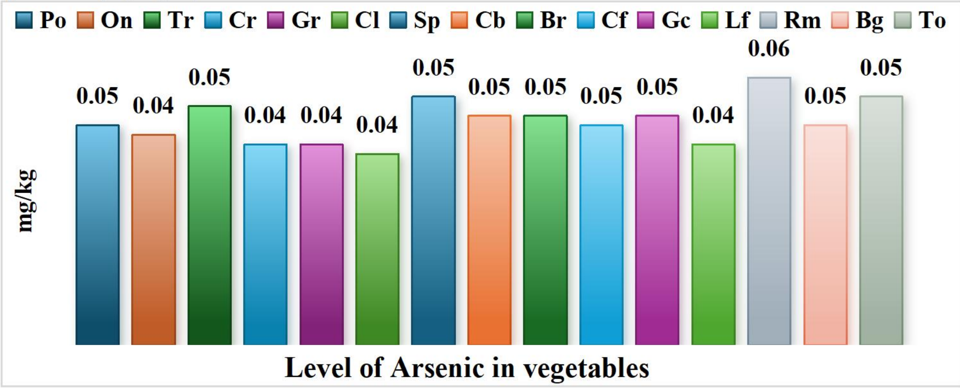

Figure 5. The concentration of arsenic in vegetables

3.2 Estimated Daily Exposure of Metals (EDEM)

EDEM is the estimated amount of a specific metal ingested daily by an individual through consumption of contaminated food, water, or other sources, normalized to body weight (mg/kg bw/day or µg/kg,bw/day). Results reported in Table 1 indicate that all the vegetable samples are < 1, which means there is no quick human threat to the local inhabitants of the study area regarding EDEM.

Table 1. Estimated Daily Intake of trace and toxic metals from vegetables (mg/kg bw/d)

Vegetable	(Cr)	(Cd)	(Cu)	(As)
Potatoes	0.00008	0.00069	0.01807	0.00011
Turnip	0.00011	0.00064	0.00459	0.00017
Onion	0.00011	0.00072	0.01231	0.00014
Carrot	0.00008	0.00007	0.00636	0.000003
Garlic	0.00014	0.00014	0.00949	0.00012
Spinaches	0.00017	0.00017	0.01051	0.00014
Coriander leaves	0.00008	0.00011	0.01270	0.00017
Cabbages	0.00011	0.00011	0.00916	0.00019
Brinjal	0.00019	0.00019	0.00032	0.00017
Cauliflower	0.00017	0.00017	0.00457	0.00011
Green chilies	0.00011	0.00011	0.00318	0.00014
Ladyfingers	0.00017	0.00017	0.00064	0.00011
Round melons	0.00014	0.00014	0.00719	0.00017
Tomatoes	0.00011	0.00011	0.01812	0.00011
Bitter gourds	0.00017	0.00017	0.00653	0.00014

3.2.1. Targeted Hazard Quotient (THQ)

The targeted hazard quotient is the ratio of exposure to the toxic element to the reference dose, which is the highest level at which no adverse health effects are expected. The THQ describes the non-carcinogenic health risk posed by exposure to the respective toxic element. The Targeted hazard quotient calculated for root, fruit, and leafy vegetables is <1, indicating no direct threat to local people in the study area (Table 2).

Table 2. Targeted Hazard Quotient (THQ) of vegetables from District Ghotki

Vegetables	(Cr)	(Cd)	(Cu)	(As)
Potatoes	0.001	0.09	0.03	0.2
Turnips	0.002	0.08	0.008	0.03
Onions	0.002	0.1	0.02	0.03
Carrots	0.002	0.09	0.01	0.0006
Garlic	0.004	0.02	0.01	0.02
Spinaches	0.001	0.01	0.02	0.03
Coriander leaves	0.002	0.01	0.01	0.03
Cabbages	0.005	0.02	0.005	0.04
Brinjals	0.001	0.02	0.007	0.02
Cauliflower	0.002	0.01	0.04	0.02
Green chilies	0.004	0.02	0.001	0.02
Ladyfingers	0.003	0.01	0.01	0.03
Round melons	0.002	0.01	0.03	0.02
Tomatoes	0.001	0.02	0.01	0.02
Bitter guards	0.004	0.02	0.04	0.02

3.2.2. The Bio-concentration Factor (BCF)

BCF is an environmental risk assessment parameter used to evaluate an organism's ability to accumulate a chemical or metal directly from its surrounding environment (such as water or soil) into its tissues. It is the ratio of the concentration of a metal or contaminant in an organism's tissues to its concentration in the surrounding environment under equilibrium conditions. Results reported in Table 3 show the concentrations of elements such as chromium, copper, and arsenic in vegetables, with copper slightly elevated in potatoes and tomatoes at 2.120 and 2.127 mg/kg, respectively.

Table 3. Bio-concentration Factor of vegetables(mg/kg).

Vegetables	(Cr)	(Cd)	(Cu)	(As)
Potatoes	0.176±0.02	0.694±0.03	2.120±0.02	0.25±0.03
Turnips	0.235±0.03	0.639±0.03	0.539±0.09	0.37±0.04
Onions	0.235±0.02	0.722±0.02	1.438±0.05	0.31±0.03
Carrots	0.176±0.01	0.667±0.02	0.747±0.07	Garlic
Garlics	0.294±0.03	0.139±0.03	1.114±0.04	0.25±0.03
Spinaches	0.353±0.03	0.167±0.04	1.234±0.06	0.31±0.03
Coriander leaves	0.176±0.03	0.083±0.03	1.490±0.07	0.37±0.03
Cabbages	0.235±0.03	0.111±0.02	1.075±0.06	0.43±0.02
Brinjal	0.412±0.01	0.194±0.02	0.380±0.06	0.37±0.03
Cauliflower	0.353±0.02	0.167±0.03	0.536±0.08	0.25±0.03
Green chilies	0.235±0.02	0.111±0.03	0.373±0.07	Ladyfingers

Ladyfingers	0.353±0.03	0.167±0.02	0.075±0.07	0.25±0.02
Round melons	0.294±0.02	0.139±0.03	0.844±0.09	0.37±0.03
Tomatoes	0.235±0.03	0.111±0.03	2.127±0.07	0.25±0.03
Bitter gourd	0.353±0.02	0.167±0.03	0.766±0.07	0.31±0.03

3.3. Pearson Correlation Coefficient of Vegetables in District Ghotki

Results showed that the strongest negative correlation, -.963**, was between coriander leaves and carrot, while round mona was positively correlated with potato at 0.903* at the 0.05 significance level. Tomato was also positively correlated with turnip at 0.950* at the 0.05 significance level.

3.3.1 Correlation Coefficient of Cu among Vegetables

Results show that cauliflower was negatively correlated with coriander leaves, with a correlation coefficient of -0.909* at the 0.05 significance level. Green chili was negatively and positively correlated with turnip (-0.887*). Similarly, tomato was strongly positively correlated with green chili, with values of 1.000** and 0.709* at the significant levels of 0.05 and 0.01, respectively. Round melon showed a positive correlation with brinjal at .896*. Similarly, the tomato showed a negative correlation with onion (-.918*) and a positive correlation with onion (.924*), respectively. The bitter guard was negatively correlated with round melons at- 932*, with respect to the copper element, as shown in Table 4.

Table 4. Linear correlation coefficient matrix of Cu among different vegetables

Vegetables	Po.	Tr.	On.	Cr.	Gr.	Sp.	Cl.	Cb.	Br.	Cf.	Gc.	Lf.	Rm.	To.	Bg.
Potatoes	1														
Turnips	.180	1													
Onions	-.513	-.519	1												
Carrots	-.039	.824	-.017	1											
Garlics	.013	.413	.481	.721	1										
Spinaches	.396	-.114	-.698	-.654	-.727	1									
Coriander L	.101	-.738	-.178	-.963**	-.867	.721	1								
Cabbages	-.627	.534	.023	.695	.205	-.545	-.606	1							
Brinjals	-.123	-.334	-.097	-.189	-.588	-.058	.381	.232	1						
Cauli flowers	-.712	-.656	.921*	-.269	.173	-.464	.085	.034	-.022	1					
Green chilies	.745	-.403	-.114	-.358	-.222	.194	.424	-.667	.388	-.266	1				
Lady fingers	-.540	-.645	.520	-.262	-.307	-.393	.299	.236	.779	.607	.142	1			
Round melons	.903*	-.147	-.453	-.447	-.248	.656	.467	-.869	-.145	-.520	.747	-.463	1		
Tomatoes	.374	.950*	-.675	.629	.287	.166	-.551	.276	-.447	-.779	-.292	-.826	.124	1	
Bitter gourds	-.615	.159	-.299	.052	-.531	.084	.105	.710	.526	-.039	-.516	.377	-.602	.039	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

3.3.2 Correlation Coefficient of Cd among vegetables

Results show that Brinjal was negatively correlated with turnip, with a correlation coefficient of -0.894* at the 0.05 significance level. Ladyfinger was also strongly positively correlated with cauliflower 1.000**); similarly, tomato was strongly negatively correlated with green chili, with a value of 1.000** at the significant levels of 0.05 and 0.01, respectively. Similarly, bitter gourd is positively correlated with carrot for cadmium, as shown in Table 5.

Table 5. Linear correlation coefficient matrix of Cadmium among different vegetables

	Tr.	On.	Cr.	Gr.	Sp.	Cl.	Cb.	Br.	Cf.	Gc.	Lf.	Rm.	To.
Potatoes													
Turnips	1												
Onions	.841	1											
Carrots	.735	.748	1										
Garlic	-.504	-.851	-.440	1									
Spinaches	-.018	.229	.543	-.050	1								
Coriander leaves	.286	.102	.578	.000	.013	1							
Cabbages	-.405	-.388	.165	.271	.233	.735	1						
Brinjals	-.894*	-.596	-.754	.238	.081	-.646	.026	1					
Cauli flowers	.038	-.366	-.166	.756	.019	-.244	-.307	-.090	1				
Green chilies	-.403	.088	-.400	-.500	.050	-.645	-.271	.715	-.567	1			
Ladyfingers	.038	-.366	-.166	.756	.019	-.244	-.307	-.090	1.000**	-.567	1		
Round melons	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	
Tomatoes	-.403	.088	-.400	-.500	.050	-.645	-.271	.715	-.567	1.000**	-.567	.[a]	1
Bitter gourds	-.164	-.657	-.363	.904*	-.318	.044	.024	-.075	.854	-.678	.854	.[a]	-.678

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

3.3.3. Linear correlation coefficient matrix of Chromium among vegetables

Cauliflower had a negative correlation with turnip, with a single star -.938*, whereas ladyfinger had a positive correlation with cauliflower, with a double star (r = 1.000*, p < 0.01; 2-tailed). The results are mentioned in Table 6

Table 6. Linear correlation coefficient matrix of Chromium among vegetables

	Po	Tr	On	Cr	Gr	Sp	Cl	Cb	Br	Cf	Gc	Lf	Rm	To	Bg
Potatoes	1														
Turnips	.681	1													
Onions	.313	.004	1												
Carrots	-.218	-.721	.225	1											
Garlic	-.423	-.620	.673	.645	1										
Spinaches	-.185	-.241	-.495	.592	-.050	1									
Coriander leaves	.873	.480	.571	.167	.000	.013	1								
Cabbages	.413	.437	.508	.210	.271	.233	.735	1							
Brinjals	-.766	-.089	-.235	-.185	.238	.081	-.646	.026	1						
Cauli F	-.479	-.938*	.324	.732	.756	.019	-.244	-.307	-.090	1					
Green chili	-.423	.310	-.704	-.645	-.500	.050	-.645	-.271	.715	-.567	1				
Lady fin	-.479	-.938*	.324	.732	.756	.019	-.244	-.307	-.090	1.000**	-.567	1			
Round me	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]	.[a]		
Tomatoes	-.423	.310	-.704	-.645	-.500	.050	-.645	-.271	.715	-.567	1.000**	-.567	.[a]	1	
Bitter gourds	-.248	-.644	.752	.554	.904*	-.318	.044	.024	-.075	.854	-.678	.854	.[a]	-.678	1

a. Cannot be computed because at least one of the variables is constant.

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

3.3.4. Linear correlation coefficient matrix of As among vegetables

Ladyfinger was negatively correlated with green chili at -0.919*, whereas bitter gourd was strongly positively correlated with round melon at 1.000*, and the correlation was significant at the 0.01 level (2-tailed), as shown in Table 7.

Table 7. Linear correlation coefficient matrix of Arsenic among different vegetables

	Po.	Tr.	On.	Cr.	Gr.	Sp.	Cl.	Cb.	Br.	Cf.	Gc.	Lf.	Rm.	To.	Bg.
Potatoes	1														
Turnips	.373	1													
Onions	-.102	.456	1												
Carrots	-.327	-.244	.535	1											
Garlic	.764	.732	.535	-.071	1										
Spinaches	.764	.732	-.134	-.429	.643	1									
Coriander	-.577	.387	.354	.378	-.189	.000	1								
Cabbages	-.490	.626	.514	.046	.046	.046	.849	1							
Brinjals	-.167	.745	.612	.327	.327	.327	.866	.840	1						
Cauliflower.	.102	.000	.250	.802	.134	.134	.354	-.086	.408	1					
Green chili	-.408	.000	-.375	.134	-.535	.134	.707	.343	.408	.375	1				
Ladyfingers	.167	-.186	.153	-.327	.218	-.327	-.722	-.315	-.583	-.663	-.919*	1			
Round m	.167	.373	-.102	-.873	.218	.218	-.289	.210	-.167	-.919*	-.408	.583	1		
Tomatoes	.644	.000	.369	.435	.639	.163	-.468	-.541	-.125	.522	-.560	.229	-.395	1	
Bitter gourd.	.167	.373	-.102	-.873	.218	.218	-.289	.210	-.167	-.919*	-.408	.583	1.000**	-.395	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

For the accuracy of the results, current data, when compared to other sophisticated machines, such as the GFAAS-800 Perkin Elmer, showed more than 90% similarity, as shown in Table 8.

Table 8. Analysis of different trace and toxic elements of Ghotki District

Element (mg/kg)	Present results	RSD%	GFAAS-800 Perkin Elmer (mg/kg)	RSD%	Recovery (%)
Mean Cu	3.46	2.61	3.41	2.31	98.55
Mean Cd	0.36	3.2	0.35	2.6	97.2
Mean Cr	0.0585	5.2	0.0568	4.5	97.10
Mean As	0.051	5.14	0.048	3.15	94.1

Furthermore, the obtained results (values) were compared with certified reference material (Standard reference material, National Institute of Standards and Technology (SRM NIST 1515) [27], recovery percent of copper Cu, Cd, Cr, and As 95.5%, 98.40%, 95.6%, and 93.8%, respectively (Table 9).

Table 9. Certified reference materials

Element	Certified values	Found values	Recovery %
Cu	3.20	3.056	95.5
Cd	0.311	0.306	98.40
Cr	0.081	0.0775	95.6
As	0.049	0.046	93.8

(Standard Reference Material National Institute of Standards and Technology) (SRM NIST 1515) data for checking Analytical accuracy

4.0 Conclusion

This study evaluated the concentrations of selected trace and toxic metals, including Cu, Cd, Cr, and As, in commonly consumed vegetables from District Ghotki, Pakistan, and assessed potential human health risks using estimated daily metal exposure, target hazard quotient, and bio-concentration factor. The results showed that copper concentration exceeded the WHO/FAO permissible limit (5 mg/kg) in potato (6.55 mg/kg) and tomato (6.54 mg/kg) samples. In contrast, the maximum concentrations of Cd, Cr, and As detected in vegetables remained within the recommended WHO/FAO limits (Cd = 0.6 mg/kg, Cr = 0.3 mg/kg, and As = 0.1 mg/kg). Although a small proportion of vegetable samples exhibited elevated concentrations of certain toxic metals, these exceedances were isolated rather than widespread. The health risk assessment further demonstrated that the estimated daily exposure of metals and target hazard quotient values for Cum Cd, Cr, and As, were all below the critical threshold of 1 (one) (THQ < 1), indicating that the current dietary exposure through vegetable consumption is unlikely to pose significant non-carcinogenic health risks to the local population. The estimated daily exposure followed the order: As < Cd < Cr < Cu, whereas soil-to-plant bio-concentration followed the reverse trend (Cu > Cr > Cd > As). The THQ values decreased in the order Cd > Cr> Cu > As, suggesting that cadmium contributed relatively more to the overall health risk, although all values remained within the safe range.

Overall, the findings indicated that consumption of vegetables cultivated in the study area does not present an immediate health risk to consumers under exposure conditions. Therefore, the potential health risks associated with dietary intake of these vegetables are of low concern. However, the occurrence of elevated metal concentration in a limited number of samples highlights the need for continuous environmental monitoring, routine surveillance of agricultural soils and vegetables, and implementation of appropriate pollution control and regulatory measures. Such proactive management strategies are essential to prevent long-term consumption of toxic metals in the food chain, safeguard public health, and ensure the sustainable production of safe vegetables in District Ghotki.

Recommendation

The outcomes of the present study emphasize the consequence of routine monitoring of trace and toxic elements in vegetables cultivated within the study area. Continuous observation is essential for evaluating potential health risks and preventing the long-term accumulation of these elements in the human food chain. Effective management and regulatory measures should be implemented to minimize environmental contamination and reduce human exposure.

Further research is warranted to identify and quantify the major sources of metal contamination, including agricultural soils, irrigation water, atmospheric deposition, and emissions from nearby industrial activities. Such investigations will support the development of targeted mitigation strategies and evidence-based environmental policies. In the provisional, consumption of vegetable species found to contain elevated concentrations of trace and toxic elements should be limited in the affected districts until appropriate remediation and risk management measures have been implemented

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