HEAVY METAL CONTAMINATION IN VEGETABLES GROWN WITH WASTEWATER IN PERI URBAN AREAS OF MULTAN CITY, PAKISTAN: A HEALTH RISK ASSESSMENT

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ABSTRACT: A study conducted in Multan, Pakistan, evaluated the risks posed by heavy metal contamination in commonly consumed vegetables cultivated using various water sources. The health risks related with heavy metal pollution in regularly consumed vegetables grown using different water sources were assessed in a study carried out in Multan, Pakistan. Using ICP-OES, cadmium (Cd), copper (Cu), manganese (Mn), chromium (Cr), nickel (Ni), and lead (Pb) were measured in 100 vegetable samples, including 30 Brassica samples. The same metals were also examined in 30 soil samples and 30 water/wastewater samples. The findings demonstrated that plants irrigated with wastewater acquired significantly more heavy metals than vegetables grown with canal or tube-well water. In contrast to vegetables cultivated using pure water sources, which had a much smaller range of accumulation factor 0.34 to 0.57, while wastewater-irrigated vegetables had an accumulation factor ranging from 2.50 to 13.74, which shows the concentration of metals in plants relative to the soil. Furthermore, vegetables that were watered with wastewater had a much higher total target hazard quotient (TTHQ) (**2.04 to 13.41**) and presented a "carcinogenic health risk" to the effected population. While vegetables cultivated with canal or tube-well water were deemed "health risk-free". Waste-water irrigation is a significant source of heavy metal pollution in soil and plants according to multivariate statistical analysis. The study emphasizes that wastewater must be treated before use in agriculture in order to reduce the health concerns related to exposure to heavy metals.

Keywords: Vegetables, wastewater irrigation, accumulation factor, total target hazard quotient, carcinogenic, health risk index, Multan city.

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INTRODUCTION

Heavy metal contamination in vegetables represents a critical environmental and public health concern in Pakistan, primarily driven by the widespread use of industrial wastewater for irrigation. Rapid industrialization and urbanization have exacerbated the problem, leading to the discharge of untreated or inadequately treated wastewater containing toxic heavy metals into water bodies and agricultural fields (Khan *et al*., 2008). Metals such as cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), and nickel (Ni) accumulate in soils and are readily absorbed by plants, including commonly consumed vegetables (Alloway, 2013). This practice, often necessitated by water scarcity and economic challenges, further aggravates the issue (Rizwan *et al*., 2016). Consuming vegetables contaminated with heavy metals poses serious health risks, including neurological damage, kidney dysfunction, developmental delays, and various forms of cancer (Järup, 2003).

The type of industrial activity discharging the wastewater, the quantity of heavy metals in the effluents, the pH and organic content of the soil, and the particular vegetable species being grown are some of the variables that affect the level of contamination. (Sharma *et al*., 2007). Addressing this issue requires regular monitoring of heavy metal levels in vegetables and the implementation of robust wastewater treatment systems to mitigate contamination risks. This study investigates the extent of heavy metal contamination in vegetables grown in Pakistan using industrial wastewater for irrigation, aiming to evaluate associated health risks and propose actionable mitigation strategies.

Heavy metal poisoning has become a rising environmental and public health concern in Pakistan due to the country's growing reliance on untreated or inadequately treated industrial wastewater for agricultural irrigation. Effluents containing high concentrations of hazardous metals like cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), nickel (Ni), and mercury (Hg) have been released into agricultural lands and water bodies as a result of rapid industrial growth and inadequate wastewater treatment infrastructure (Ahmad *et al*., 2018). These metals persist in the soil and are readily absorbed by plants through their roots, leading to bioaccumulation in edible vegetable tissues and posing direct health risks to consumers (McLaughlin *et al*., 1999; Zhuang *et al*., 2009).

In water-scarce regions of Pakistan, particularly arid and semi-arid areas, the use of industrial wastewater for irrigation is often a necessity due to limited access to alternative water sources and economic constraints faced by farmers (Qureshi *et al*., 2016). While this practice temporarily alleviates water shortages, it creates a significant pathway for heavy metal contamination to enter the food chain. Prolonged exposure to these metals through dietary intake has been associated with severe health issues, including neurological impairments, kidney damage, cardiovascular diseases, developmental abnormalities, and various cancers (Tchounwou *et al*., 2012). This study seeks to evaluate the scale of heavy metal contamination in vegetables irrigated with industrial wastewater, assess the associated health risks, and recommend effective measures to protect public health and ensure sustainable agricultural practices

The extent of contamination and the specific heavy metals present are influenced by factors such as the type of industrial activities in the area, the composition of wastewater, soil characteristics (e.g., pH and organic matter content), and the types of vegetables grown (Wuana & Okieimen, 2011). Tackling this issue necessitates comprehensive monitoring of heavy metal concentrations in both wastewater and vegetables, coupled with the adoption of advanced wastewater treatment technologies and sustainable farming practices. This study examines the degree of heavy metal contamination in vegetables irrigated with industrial wastewater across various regions in Pakistan. It evaluates the associated health risks and offers evidence-based recommendations for policy changes and mitigation measures to protect public health.

Copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni), mercury (Hg), and lead (Pb) are frequent harmful heavy metal found in wastewater, a complex mixture of household, industrial, and agricultural effluents. The usage of waste water for irrigation has grown in popularity due to water constraint, particularly in developing nations. Wastewater is being used to irrigate over 20 million hectares of land worldwide, or 7% of all cultivated land. This method is more common in Pakistan. Untreated or incompletely treated waste water is used to serve around 800,000 hectares of land either directly or indirectly.

Heavy metal contamination in soil and crops is due to the uncontrolled use of wastewater in agriculture. After entering the food chain, these metals can seriously harm people's health by causing problems with the liver, kidneys, heart, bones, and neurological system.

To address these risks, implementing effective wastewater treatment and disposal systems is essential. Proper treatment can substantially reduce heavy metal concentrations and other pollutants in wastewater, making it safer for agricultural use. Additionally, regular monitoring of soil and water quality is crucial to evaluate contamination levels and implement corrective measures.

Rapid urbanization and industrialization are causing major environmental problems for Pakistan's historic city of Multan. More than 200 industrial facilities spread across 1,300 acres of the Multan Industrial Estate release untreated wastewater into the nearby sewer system. Concerns regarding heavy metal poisoning of crops are raised by the regular use of this effluent for irrigation in nearby locations.

This study aimed to evaluate the concentrations of heavy metals (Cd, Cr, Cu, Mn, Ni, and Pb) in vegetables grown in Multan using different water sources. The objectives included analyzing the accumulation of these metals in vegetables and assessing the related health risks. The findings offer valuable insights for policymakers to formulate strategies that safeguard public health while mitigating the environmental and health impacts of wastewater irrigation.

MATERIALS AND METHODS

Study Area: The study was accompanied in six peri-urban irrigation sites in Multan, a region renowned for its agricultural production of vegetables, wheat, fruits, fodder, milk, and meat. These sites were selected to represent various irrigation sources, including untreated industrial effluent, untreated urban wastewater, a combination of canal water and untreated wastewater, canal water, and tube well water. One site, historically irrigated with treated urban wastewater, was categorized as a tube well water site for this study.

Soil and water samples were taken from each location to assess how various irrigation sources affected the levels of heavy metal contamination. From these sites, 100 vegetable samples were also collected, 30 of which were Brassica samples. Optical Emission Spectrometry

(ICP-OES) analysis were performed to test the samples for lead (Pb), nickel (Ni), manganese (Mn), copper (Cu), cadmium (Cd), and chromium (Cr).

By comparing the effects of various irrigation sources and examining heavy metal deposition in soil and plants, this study sought to shed light on the possible health consequences of eating vegetables cultivated with contaminated water.

Diurnal Intake of Heavy Metals via Vegetables: An average person weight of 60 kg and a daily consumption of 0.527 kg of green vegetables per person were taken into account for calculation of the Daily Intake of Metals (DIM). Using a conversion factor of 0.085, the dry weight concentration (of heavy metals) in vegetables was taken as fresh weight.

Each metal's daily intake was divided by its corresponding oral reference dose (RfD) to calculate the Health Risk Index (HRI). Cadmium, chromium, copper, manganese, nickel, lead, and cadmium RfD values were sourced from the US EPA's Integrated Risk Information System (IRIS). The Total Target Hazard Quotient (TTHQ) was computed by adding the individual HRIs in order to assess the combined health risk from several metal. A TTHQ value below 1.0 indicates negligible health risks, whereas a value exceeding 1.0 suggests potential health concerns.

Statistical Analyses: Statistical methods such as ANOVA, Pearson correlation matrix, principal component analysis (PCA), and hierarchical cluster analysis (HCA) were employed to determine the reasons for heavy metal contamination in vegetables and to understand the relationships between various factors. These analyses provided valuable insights into the factors influencing contamination and helped quantify the associated health risks.

RESULTS

Heavy Metal testing in waste-water Used for Irrigation Across Six Sites: Heavy metal concentrations in irrigation water and effluent from six locations were measured, and mean values and standard deviations were reported. The Pearson correlation was used to determine the relationship between the concentrations of heavy metals in wastewater, soil, and vegetables (Brassica) in order to assign source attribution. The site-wise order of total heavy metal concentrations in wastewater was as follows:
Site-I (0.790 mg/L) > Site-IV (0.548 mg/L) > Site-VI (0.465 mg/L) > Site-II (0.403 mg/L) > Site-III (0.157 mg/L) > Site-V (0.011 mg/L). These results revealed that wastewater contained significantly higher levels of heavy metals than canal and tube well water.

Total Heavy Metal testing in Soil Across Six Irrigation Sites: The total heavy metal concentrations in surface soils at Site-I, II, III, IV, V, and VI were 313.9, 172.6, 142.7, 152.7, 118.7, and 141.2 mg/kg, respectively. The ranking of total heavy metal contamination in soils was: Site-I > Site-II > Site-IV > Site-III > Site-VI > Site-V. Soils at Sites-I, II, III, IV, and VI were 2.64, 1.45, 1.20, 1.28, and 1.17 times more contaminated than those at Site-V (control area). The outcomes revealed that soils irrigated with wastewater were more heavily contaminated as compared to those irrigated with canal or tube well water.

Heavy Metal testing in Vegetables Across Six Sites: The average levelof heavy metals in Brassica across the six sites are summarized below:

- **Cadmium (Cd):** The mean Cd levels were 1.74, 0.28, 0.55, 0.416, 0.034, and 0.056 mg/kg at Sites I, II, III, IV, V, and VI, respectively. These values surpassed the prescribed limit of 0.02 mg/kg (Balkhair & Ashraf, 2016; WHO/FAO, 1995) across all sites. Cd levels were 87, 14, 27.5, 21, 1.7, and 2.8 times higher than the limit at Sites I, II, III, IV, V, and VI, respectively.

- **Chromium (Cr):** The mean Cr levels were 4.67, 4.46, 7.54, 4.56, 0.194, and 0.63 mg/kg at Sites I, II, III, IV, V, and VI, respectively. Cr levels surpassed the prescribed limit of 0.2 mg/kg except at Site-V.

- **Copper (Cu):** The mean Cu levels were 19.7, 16.5, 25.01, 18.62, 0.086, and 0.022 mg/kg at Sites I, II, III, IV, V, and VI, respectively. These values surpassed the prescribed limit of 0.1 mg/kg at Sites I, II, III, and IV.

- **Manganese (Mn):** The mean Mn levels were 69.27, 28.0, 74.05, 26.2, 2.28, and 3.6 mg/kg at Sites I, II, III, IV, V, and VI, respectively. These values were significantly higher than the prescribed limit of 0.3 mg/kg.

- **Nickel (Ni):** The mean Ni levels were 3.2, 3.04, 4.4, 3.1, 1.18, and 3.12 mg/kg at Sites I, II, III, IV, V, and VI, respectively. These values surpassed the prescribed limit of 0.1 mg/kg.

Lead (Pb) Levels in Brassica: The mean Pb concentrations in Brassica (Table 2) were 4.53, 3.864, 2.6, 4.434, 0.214, and 0.0414 mg/kg at Sites I, II, III, IV, V, and VI, respectively. These values surpassed the WHO/FAO prescribed limit of 0.1 mg/kg at all sites except Site-VI. Pb levels were found to be 45, 39, 29, 44, and 2 times higher than prescribed limits at Sites I, II, III, IV, and V, respectively. Pb concentrations were lowest and within prescribed limits at Site-VI, while Site-VI showed slightly higher levels compared to Site-V, likely due to provision of treated waste-water since 2016.

Heavy Metal Concentrations in Brinjal (Solanum melongena) at Sites II and III: The average levelof Cd, Cr, Cu, Mn, Ni, and Pb in Brinjal at Site-II were 0.284, 5.77, 31.52, 33.17, 0.47, and 1.32 mg/kg, respectively, all exceeding WHO/FAO prescribed limits. At Site-III, the respective concentrations were 0.21, 2.91, 24.95, 20.17, 1.29, and 1.5 mg/kg, also exceeding critical limits. Cd, Cr, Cu, and Mn levels were lower at Site-III compared to Site-II, while Ni and Pb levels were higher. The total heavy metal content was 72.534 mg/kg at Site-II and 51.03 mg/kg at Site-III, far exceeding the critical limit of 0.82 mg/kg. Brinjal grown at both waste-water-irrigated sites was heavily contaminated with heavy metals.

Heavy Metal Concentrations in Spinach (Spinacia oleracea) at Sites II, III, and IV: The average levelof Cd, Cr, Cu, Mn, Ni, and Pb in Spinach at Site-II were 0.257, 5.55, 32.02, 54.47, 1.27, and 7.07 mg/kg, respectively, exceeding WHO/FAO limits. At Site-III, the respective concentrations were 0.21, 10.31, 18.4, 115.85, 4.4, and 4.4 mg/kg. At Site-IV, the concentrations were 0.465, 0.725, 13.85, 28.95, 0.32, and 1.1 mg/kg. Total heavy metal concentrations were 100.64 mg/kg, 153.57 mg/kg, and 45.41 mg/kg at Sites II, III, and IV, respectively, far above the critical limit of 0.82 mg/kg. Spinach from all three waste-water-irrigated sites was highly contaminated.

Heavy Metal Concentrations in Coriander (Coriandrum sativum) at Sites II and III: The average level of Cd, Cr, Cu, Mn, Ni, and Pb in Coriander at Site-II were 0.42, 12.2, 122.12, 69.26, 8.94, and 5.78 mg/kg, respectively, exceeding WHO/FAO prescribed limits. At Site-III, the respective concentrations were 0.41, 11.88, 120.85, 67.96, 8.04, and 5.1 mg/kg. Total heavy metal contents were 218.73 mg/kg at Site-II and 214.24 mg/kg at Site-III, significantly exceeding the critical limit of 0.82 mg/kg. Coriander from both sites was heavily contaminated.

Heavy Metal Concentrations in Cauliflower (Brassica oleracea) at Sites III and IV: The average levelof Cd, Cr, Cu, Mn, Ni, and Pb in Cauliflower at Site-III were 0.148, 5.57, 19.35, 29.65, 1.02, and 0.6 mg/kg, respectively, exceeding WHO/FAO critical limits. At Site-IV, the respective concentrations were 0.2, 5.49, 20.54, 28.06, 2.98, and 4.6 mg/kg. Total heavy metal contents were 56.338 mg/kg at Site-III and 61.87 mg/kg at Site-IV, far exceeding the critical limit of 0.82 mg/kg. Cauliflower from both sites was highly contaminated with heavy metals.

Heavy Metal Concentrations in Carrot (Daucus carota) at Site III: The average levelof Cd, Cr, Cu, Mn, Ni, and Pb in Carrot at Site-III were 0.162, 5.69, 16.42, 35.9, 1.44, and 4.5 mg/kg, respectively, all exceeding WHO/FAO prescribed limits. Total heavy metal content in Carrot was 54.112 mg/kg, far above the critical limit of 0.82 mg/kg. Carrots grown at the waste-water irrigation site were heavily contaminated.

Heavy Metal Concentrations in Onion (Allium cepa) at Site III: The average levelof Cd, Cr, Cu, Mn, Ni, and Pb in Onion at Site-III were 0.21, 3.97, 21.47, 30.2, 2.28, and 1.4 mg/kg, respectively, exceeding WHO/FAO critical limits. Total heavy metal content in Onion was 59.53 mg/kg, well above the critical limit of 0.82 mg/kg. Onions grown at the waste-water irrigation site were highly contaminated

Heavy Metal Concentration in Potato (Solanum tuberosum) at Sites IV and VI: The results (Table 2) revealed that the average levelof Cd, Cr, Cu, Mn, Ni, and Pb in potatoes at Site-IV were 0.38, 0.17, 11.55, 0.396, 0.27, and 1.048 mg/kg, respectively, with all metals exceeding the WHO/FAO critical limits, except for Cr, which was slightly below the limit. At Site-VI, the average levelof Cd, Cr, Cu, Mn, Ni, and Pb were 0.062, 0.11, 0.0264, 3.69, 0.137, and 0.0216 mg/kg, respectively. The concentrations of Cu, Mn, and Ni were slightly above the critical limits at Site-VI, while Cr, Cu, and Pb were below the limits. Total heavy metal content in potatoes at Site-IV and Site-VI was 13.816 and 4.047 mg/kg, respectively, both exceeding the WHO/FAO critical limit of 0.82 mg/kg for the examined metals. The total metal content in potatoes at Site-VI was about one-third that at Site-IV, likely due to the short-term use of treated waste-water at Site-VI since June 2016, compared to the long-term use of untreated waste-water at Site-IV for the past 25 years. Potatoes grown at both waste-water-irrigated sites were found to be heavily contaminated with heavy metals.

Heavy Metal Concentration in Pea (Pisum sativum) Seeds at Site-VI: The mean quantities of Cd (0.022 mg/kg), Cr (0.629 mg/kg), Cu (0.0216 mg/kg), Mn (3.76 mg/kg), Ni (0.31 mg/kg), and Pb (0.0118 mg/kg) were found in pea seeds at Site-VI, according to the results (Table 2). While Cu and Pb concentrations were within allowable bounds, those of Cd, Cr, Mn, and Ni marginally above the WHO/FAO critical limits. However, the WHO/FAO total metals critical limit of 0.82 mg/kg was greatly surpassed by the total heavy metal level of 4.784 mg/kg in pea seeds at Site-VI. Vegetables irrigated with treated waste-water had metal contamination levels beyond allowable limits, as seen by the high levels of heavy metal contamination found in peas cultivated with treated waste-water at Site-VI. A comparison of individual metal contents in vegetables across the sites is provided in Table 2 and Figure 3. The results showed that levels of Cd, Cu, Mn, Ni, Cr and Pb surpassed prescribed limits at four waste-water-irrigated sites, with the highest values observed, while the lowest concentrations were found in vegetables watered with canal and tube-well water.

Comparison of Total Heavy Metal Concentrations in Vegetables Across Six Sites: The results (Table 2) showed the following total heavy metal concentrations in various vegetables across the six sites:

- **Brassica** at Site-I: 100.23 mg/kg
- **Brinjal** at Site-II: 72.534 mg/kg
- **Spinach** at Site-II: 100.637 mg/kg
- **Coriander** at Site-II: 218.73 mg/kg
- **Brassica** at Site-III: 53.403 mg/kg
- **Cauliflower** at Site-III: 56.338 mg/kg
- **Carrot** at Site-III: 64.112 mg/kg
- **Spinach** at Site-III: 153.572 mg/kg
- **Onion** at Site-III: 59.53 mg/kg
- **Coriander** at Site-III: 214.24 mg/kg
- **Brinjal** at Site-III: 51.03 mg/kg
- **Spinach** at Site-IV: 45.41 mg/kg
- **Potato** at Site-IV: 13.816 mg/kg
- **Cauliflower** at Site-IV: 61.87 mg/kg
- **Brassica** at Site-IV: 54.54 mg/kg
- **Brassica** at Site-V: 2.7514 mg/kg (control area)
- **Potato** at Site-VI: 4.047 mg/kg
- **Pea** at Site-VI: 4.784 mg/kg
- **Brassica** at Site-VI: 4.6614 mg/kg

The content of total heavy metal was highest in **Coriander** at Site-II and Site-III (218.73 mg/kg and 214.24 mg/kg, respectively), followed by **Spinach** (153.572 mg/kg at Site-III and 100.637 mg/kg at Site-II). The uptake of total heavy metals in **Brassica** was 114.45 mg/kg at Site-III and 100.23 mg/kg at Site-I. Leafy vegetables showed the highest uptake of total heavy metals. The lowest uptake was observed in **Brassica** at Site-V (control area) with 2.75 mg/kg, and in **Potato** (4.04 mg/kg), **Pea** (4.78 mg/kg), and **Brassica** (4.66 mg/kg) at Site-VI. The uptake of heavy metals at Site-VI was higher than at Site-V, likely due to the use of treated waste-water since June 2016. Vegetables grown at waste-water-irrigated sites (Sites I, II, III, IV) had metal contents ranging from 17 to 267 times the permissible total metals limit (0.82 mg/kg). Brassica at Site-V had contamination 3.3 times above the prescribed limit, the lowest contamination across all sites. Vegetables grown at canal water sites had less contamination compared to those grown at waste-water-irrigated sites.

Accumulation Factor (AF) of Heavy Metals in Vegetables Across Six Sites: The accumulation factor (AF) of heavy metals in crops and vegetables grown at six irrigation sites is shown in Figure 1. The results indicated that vegetables and crops grown at waste-water irrigation sites (I, II, III, IV) had total AF values ranging from 1.66 to 13.74. The highest AF values were observed in **Coriander** at Site-III (13.74) and Site-B (13.09). **Brassica** at Site-III had an AF of 7.40, and **Spinach** had an AF of 6.25 at Site-III. The AF values for **Pea** and **Potato** at Site-VI were slightly higher than at Site-V, due to the application of treated waste-water since June 2016. The total AF at Site-V and Site-VI ranged from 0.24 to 0.61, the lowest AF values. The AF for **Maize** at Site-VI was the lowest among all crops. The data suggests that crops and vegetables grown at waste-water-irrigated sites accumulated higher concentrations of heavy metals than those grown at canal water irrigation sites.

Health Risk Index (HRI) assessment and Total Target Hazard Quotient (TTHQ) for Heavy Metals in Vegetables: To determine whether the vegetables posed a health risk to the exposed population, the Total Target Hazard Quotient (TTHQ) was calculated using the Daily Intake of Metals (DIM) and Health Risk Index (HRI) values. Figure 2 compares the TTHQ values for all the heavy metals in vegetables grown at six irrigation sites for both adults and children. The results for each vegetable are described below:

- **TTHQ for Brassica:** The TTHQ for Brassica at Site-I ranged from 7.53 to 9.043, at Site-II from 3.974 to 4.769, at Site-III from 7.52 to 9.02, at Site-IV from 4.166 to 5.0, at Site-V from 0.204 to 0.245, and at Site-VI from 0.413 to 0.496. Brassica grown at Site-I, II, III, and IV presented a carcinogenic health risk (TTHQ > 1.0), while Brassica at Site-V and Site-VI posed no health risk (TTHQ < 1.0).

- **TTHQ for Brinjal (Solanum melongena):** The TTHQ value of Brinjal at Site-II ranged from 4.324 to 4.77, and at Site-III from 2.803 to 3.364. Brinjal grown at these sites exhibited carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Coriander (Coriandrum sativum):** The TTHQ value for Coriander at Site-II ranged from 10.94 to 13.13, and at Site-III from 10.578 to 12.69. Coriander grown at these sites posed a carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Spinach (Spinacia oleracea):** The TTHQ value for Spinach at Site-II ranged from 6.66 to 7.99, at Site-III from 10.39 to 12.47, and at Site-IV from 2.58 to 3.1. Spinach grown at these sites presented a carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Carrot (Daucus carota):** The TTHQ value for Carrot at Site-III ranged from 4.79 to 5.75, indicating a carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Cauliflower (Brassica oleracea):** The TTHQ for Cauliflower at Site-III ranged from 3.62 to 4.34, and at Site-IV from 4.5 to 5.4. Cauliflower grown at these sites posed a carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Onion (Allium cepa):** The TTHQ value for Onion at Site-III ranged from 3.55 to 4.26, indicating a carcinogenic health risk (TTHQ > 1.0).

- **TTHQ for Pea (Pisum sativum) Seeds:** The TTHQ value for Pea (seeds) at Site-VI ranged from 0.391 to 0.469, indicating a non-carcinogenic health risk (TTHQ < 1.0).

- **TTHQ for Potato (Solanum tuberosum):** The TTHQ value for Potato at Site-IV ranged from 0.8 to 0.96, and at Site-VI from 0.282 to 0.338. Both sites showed non-carcinogenic health risks, although the TTHQ at Site-IV was near the threshold, suggesting it could be treated as a potential carcinogenic health risk.

Hierarchical Cluster Analysis (HCA)

- **HCA of Metals in Waste-water Across Six Sites:** The dendrogram showed that metals in waste-water formed two groups: Group 1 (Cd, Cu, Mn, Ni, Pb) and Group 2 (Cr). This suggests a common source for Group 1, while Cr likely originates from the leather tanning process, as several tanneries are located in the study area.

- **HCA of Metals in Surface Soil Across Six Sites:** The dendrogram indicated two groups in surface soil: Group 1 (Cd, Pb, Cr, Cu) and Group 2 (Ni, Mn), with a common source for metals in each group.

- **HCA of Metals in Brassica Across Six Sites:** The dendrogram revealed two groups in Brassica: Group 1 (Cd, Pb, Mn, Cu, Cr) and Group 2 (Ni), suggesting that metals in Group 1 share a common source, while Ni has a different source.

Principal Component Analysis (PCA) of Heavy Metals in Brassica Across Six Sites: Two principal components (PCs) were found to have eigenvalues higher than 1.0: 71.6% of the variance was explained by PC1 (Eigenvalue 4.30), whereas 19.5% was explained by PC2 (Eigenvalue 1.17). While PC2 displayed positive loadings for Cd and Pb, suggesting a different source, PC1 displayed positive loadings for Cr, Cu, and Mn, suggesting they originate from a similar source. In accordance with the results of the HCA dendrogram, the PCA biplot verified that Cd, Pb, Mn, Cu, and Cr constitute one group and Ni forms another. The results suggest that the main sources of contamination are anthropogenic, such as industrial, commercial, and domestic waste.

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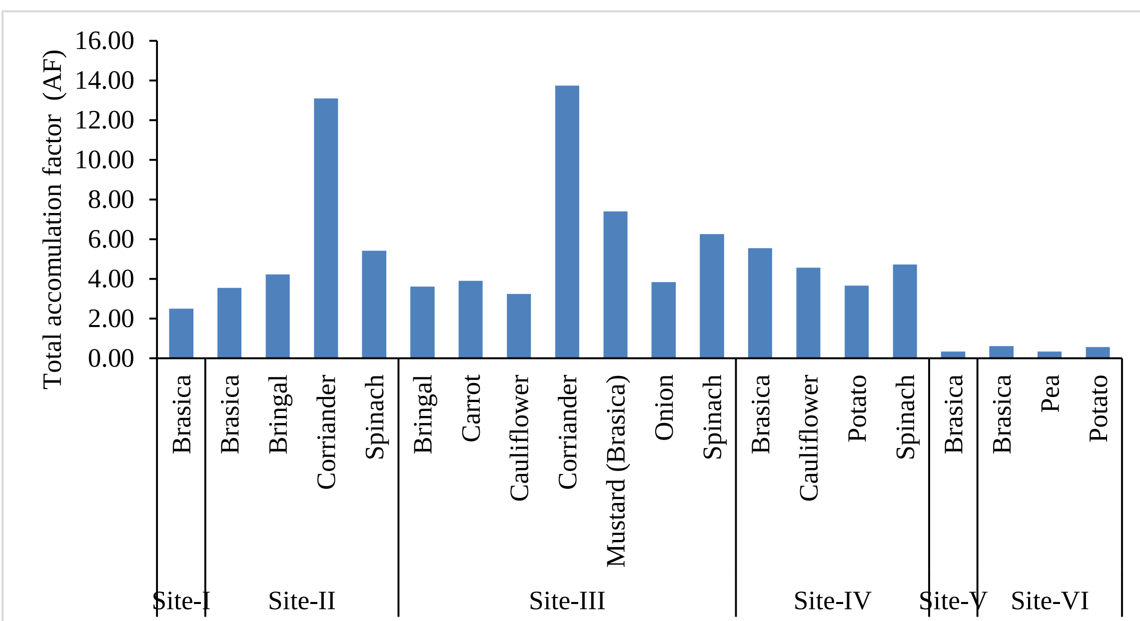

Figure 1: Site wise comparison of accumulation factor (AF) of heavy metals in vegetables grown at six irrigation sites in peri urban areas of Multan.

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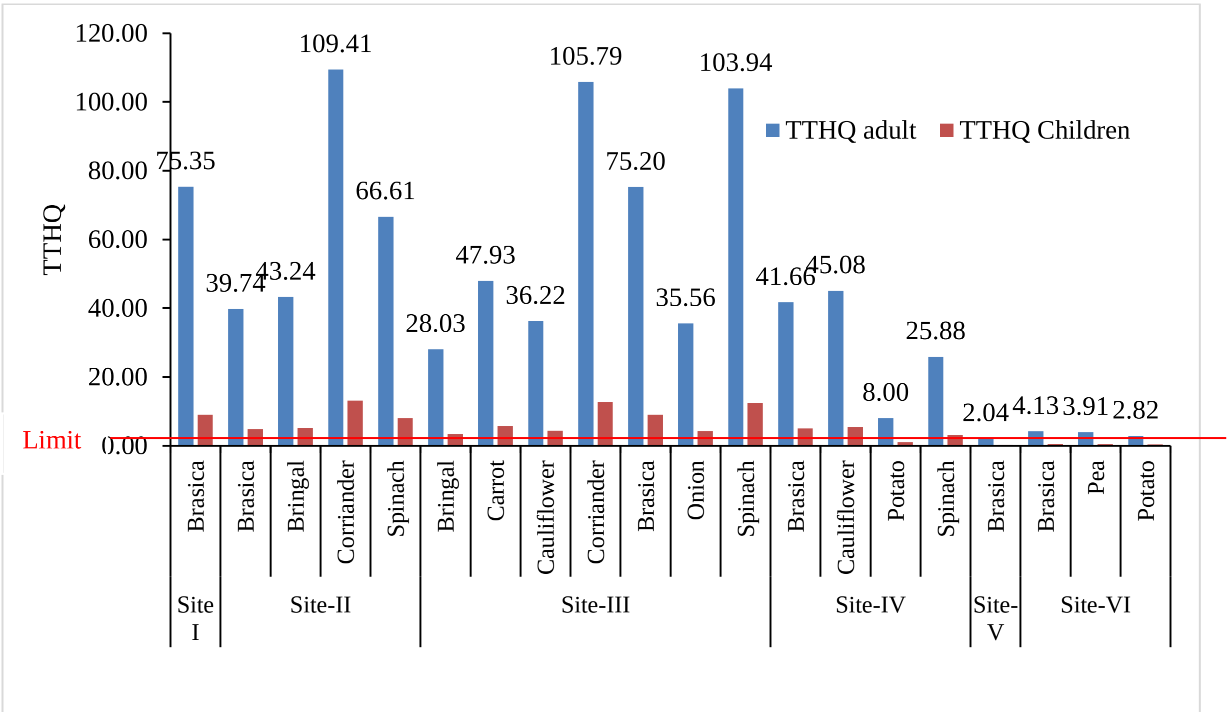

Figure 2: Site wise comparisons of TTHQ values for adults and children of heavy metals in vegetables grown at six irrigation sites in peri urban areas of Multan.

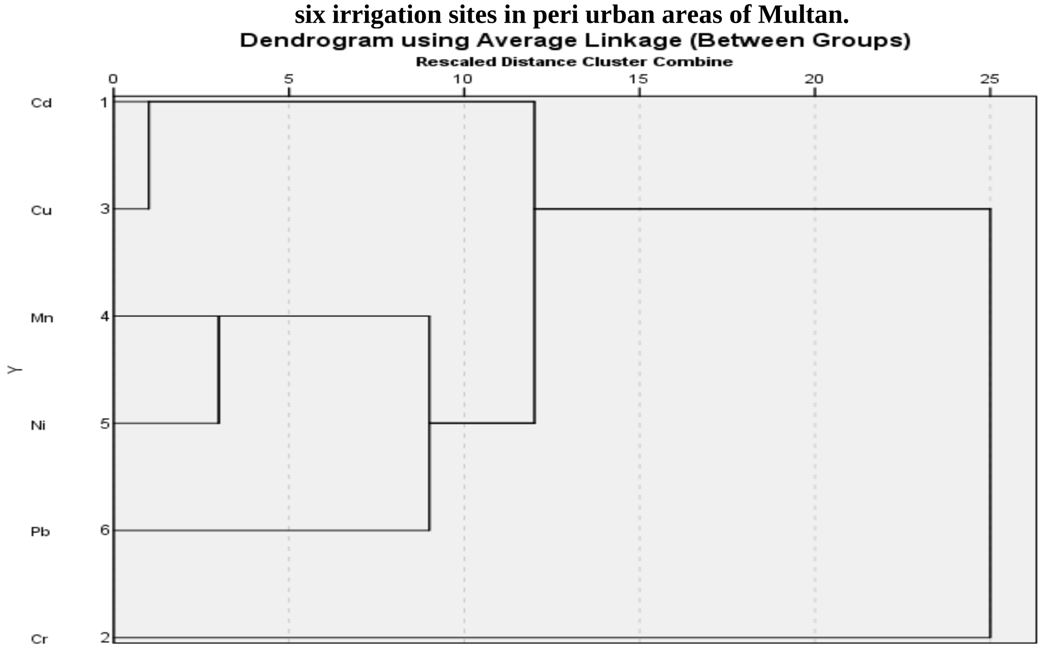

Figure 3. HCA of heavy metals in wastewater across six irrigation sites.

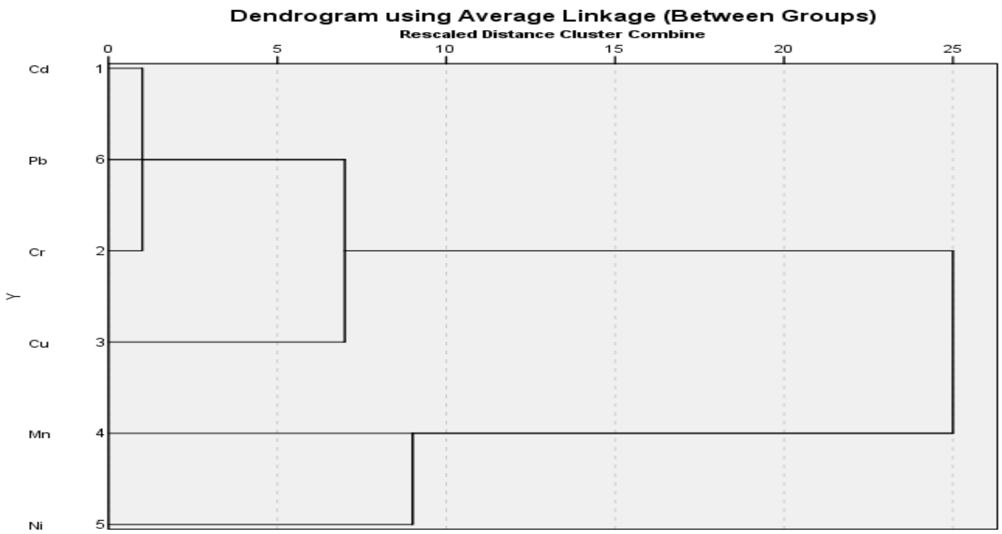

Figure 4. HCA of heavy metals in soil across six irrigation sites

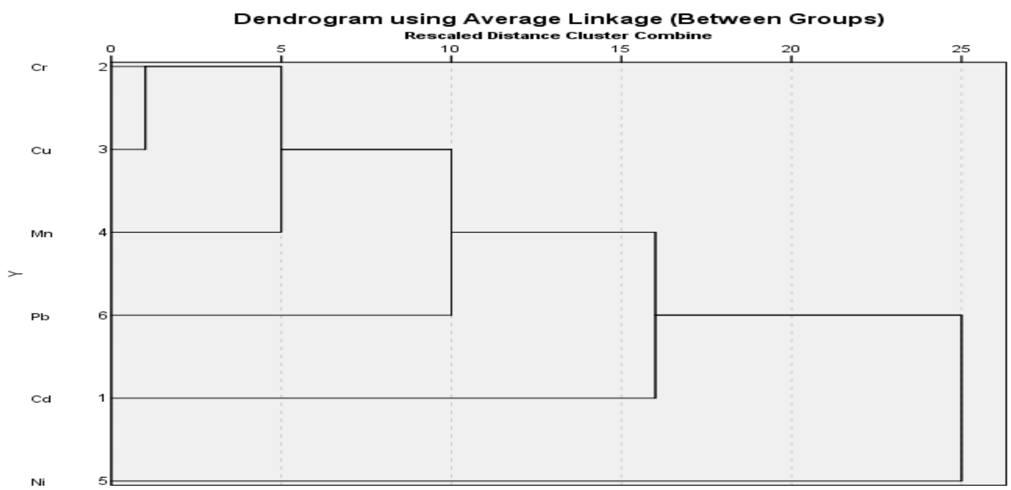

Figure 5. HCA of heavy metals in Brassica across six irrigation sites.

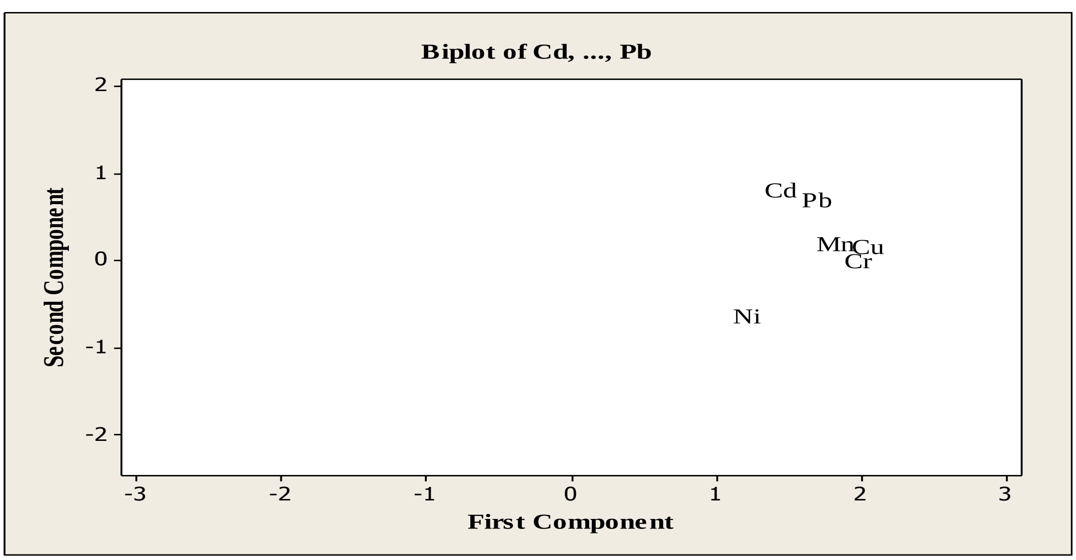

Figure 6: Principal Component Analysis of heavy metals in Brasica across six sites.

Table 1 Detail of selected sites and vegetable samples across six irrigations sites in peri urban areas of Multan.

Sr No	Name of Site	Type of wastewater	Vegetable sample	GPS coordinates	
				Latitude	Longitude
1	Site-I (Basti Valvit)	Untreated industrial effluents	*Brassica*	30.1303	71.3454
2	Site-II (Chah Bahadwala)	Untreated urban wastewater	Brinjal (*Solanum melongena*)	30.1868	71.5198
			Spinach (*Spinacia oleracea*)	30.1867	71.5196
			Coriander (*Coriandrum sativum*)	30.1861	71.5182
			Brassica	30.1864	71.5189
3	Site-III (Mouza Kayianpur)	Canal water mixed with urban wastewater	Cauliflower (*Brassica oleracea*)	30.1410	71.4484
			Carrot (*Daucus carota*)	30.1389	71.4471
			Spinach (*Spinacia oleracea*)	30.1372	71.4462
			Onion (*Allium cepa*)	30.14095	71.4484
			Coriander (*Coriandrum sativum*)	30.1384	71.4461
			Brinjal (*Solanum melongena*)	30.1371	71.4454
			Brassica	20.1353	71.4453
4	Site-IV (Binda Sandeela Suraj Myni)	Untreated urban wastewater	Spinach (*Spinacia oleracea*)	30.2337	71.4156
			Potato (*Solanum tuberosum*)	30.2384	71.4118
			Cauliflower (*Brassica oleracea*)	30.2365	71.4111
			Brassica	30.2315	71.4191
5	Site-V (Qadirpur Ranwaan)	Canal water (control area)	*Brassica*	30.3009	71.6849
6	Site-VI (Mouza Binda Mallana)	Tube well water	Potato (*Solanum tuberosum*)	30.2291	71.3910
			Pea (*Pisum sativum*)	30.2284	71.3889
			Brassica	30.2282	71.3785

Table 2. Average levelof heavy metals (mg kg^{-1}) in vegetables grown at six irrigation sites in peri urban areas of Multan city.

Name of site	Vegetables	Cd		Cr		Cu		Mn		Ni		Pb		Total metals
		Mean	± SD	Mean	± SD	Mean	± SD	Mean	± SD	Mean	± SD	Mean	± SD	
Site-I	*Brassica*	1.74	0.0316	4.67	0.0696	19.7	0.1696	69.27	1.8568	0.32	0.0394	4.53	0.0771	100.23
	Brassica	1.74	0.0316	4.67	0.0696	19.7	0.1696	69.27	1.8568	0.32	0.0394	4.53	0.0771	100.23
	Brinjal	0.284	0.0107	5.77	0.0745	31.52	0.0543	33.17	0.0308	0.47	0.0583	1.32	0.0515	72.534
Site-II	Spinach	0.257	0.0101	5.55	0.0548	32.02	0.0158	54.47	0.0381	1.27	0.0224	7.07	0.0141	100.64
	Coriander	0.42	0.0071	12.2	0.0187	122.1	0.0158	69.26	0.1051	8.94	0.0424	5.78	0.0548	218.73
	Brassica	0.28	0.0158	4.46	0.0469	16.5	0.1327	28	1.5811	0.3	0.0152	3.86	0.0932	53.408
	Cauliflower	0.148	0.0025	5.57	0.0339	19.35	0.0292	29.65	0.0187	1.02	0.0187	0.6	0.0967	56.338
	Carrot	0.162	0.0066	5.69	0.1736	16.42	0.0806	35.9	0.4950	1.44	0.1010	4.5	0.2739	64.112
	Spinach	0.21	0.0447	10.3	0.0418	18.4	0.2236	115.9	0.1224	4.4	0.4101	4.4	0.4313	153.57
Site-III	Onion	0.21	0.0430	3.97	0.1488	21.47	0.3920	30.2	0.0951	2.28	0.1105	1.4	0.1871	59.53
	Coriander	0.41	0.0803	11.9	0.2832	120.9	0.5590	67.96	0.2980	8.04	0.2074	5.1	0.2856	214.24
	Brinjal	0.21	0.0354	2.91	0.1712	24.95	0.3202	20.17	0.3885	1.29	0.1063	1.5	0.1581	51.03
	Brassica	0.55	0.0652	7.54	0.2140	25.01	0.0638	74.05	0.0316	4.4	0.2121	2.9	0.2739	114.45
Site-IV	Spinach	0.465	0.0229	0.73	0.0637	13.85	0.2500	28.95	0.3640	0.32	0.2280	1.1	0.1556	45.41

	Potato	0.38	0.0071	0.17	0.0071	11.55	0.0363	0.396	0.0114	0.27	0.0071	1.05	0.0217	13.816
	Cauliflower	0.2	0.0616	5.49	0.1769	20.54	0.1325	28.06	0.4072	2.98	0.2005	4.6	0.2550	61.87
	Brassica	0.416	0.0207	4.56	0.0316	18.62	0.0778	26.2	1.4832	0.31	0.0071	4.43	0.0654	54.54
Site-V	*Brassica*	0.034	0.0114	0.02	0.0056	0.086	0.0114	2.28	0.2280	0.12	0.0148	0.21	0.0195	2.7514
	Potato	0.062	0.0795	0.11	0.0071	0.026	0.0036	3.69	0.0071	0.14	0.0007	0.02	0.0033	4.047
Site-VI	Pea	0.022	0.0033	0.63	0.0007	0.022	0.0033	3.76	0.0071	0.34	0.0071	0.01	0.0030	4.784
	Brassica	0.056	0.0114	0.63	0.0187	0.022	0.0045	3.6	0.1581	0.31	0.0084	0.04	0.0041	4.6614
[a] Critical limits		0.02		0.2		0.1		0.3		0.1		0.1		0.82

a WHO/FAO (1995), Bulkhair and Ashraf (2015)

Table 3. Principal component loadings of selected heavy metals in wastewater, surface soil and Brassica samples.

	Wastewater		***Surface soil***	***Brassica***	
	PC1	***PC2***	***PC1***	***PC1***	***PC2***
Eigenvalues	3.67	1.39	4.29	4.30	1.17
% Total Variance	61.1	23.2	71.5	71.6	19.5
% Cumulative Variance	61.1	84.4	71.5	71.6	91.1
Cd	0.466	0.16	0.474	0.338	0.505
Cr	0.175	-0.776	0.475	0.462	-0.193
Cu	0.401	0.404	0.291	0.471	-0.022
Mn	0.51	-0.045	-0.388	0.461	-0.052
Ni	0.441	-0.383	-0.3	0.283	-0.735
Pb	0.37	0.245	0.474	0.397	0.404

DISCUSSION

The findings of this study demonstrate that vegetables grown at wastewater-irrigated sites present a "cancer-causing health risk" to individuals of all age groups, from children to adults, and are deemed unsuitable for human consumption. In contrast, vegetables irrigated with canal and tubewell water were categorized as "health risk-free" for all age groups. Among the analyzed vegetables, leafy varieties exhibited the highest carcinogenic health risks. Multivariate statistical analysis further confirmed that wastewater irrigation significantly contributes to soil and vegetable contamination.

In a related investigation of industrial effluent contamination in soil and groundwater in Multan, Pakistan, Tariq *et al*. (2010) reported average concentrations of heavy metals in industrial effluents as 0.10 mg/L for Cd, 209 mg/L for Cr, 4.65 mg/L for Ni, and 0.97 mg/L for Pb, which were higher than the levels found in this study. For soil contamination, mean concentrations were recorded as 2.64 mg/kg for Cd, 476 mg/kg for Cr, 54.5 mg/kg for Ni, and 20.2 mg/kg for Pb. While Cr and Ni levels were higher than those observed in this study, Cd and Pb concentrations were lower. These findings align with the present study's results, emphasizing the role of industrial wastewater in environmental contamination, particularly in soil.

Randhawa *et al*. (2014) conducted a study in Multan to assess heavy metal concentrations in vegetables, soil, and irrigation water. Their research revealed that metals such as Mn, Co, Ni, Cd, Cu, and Pb in irrigation water exceeded WHO/FAO permissible limits. Additionally, Cd and Pb levels in vegetables surpassed WHO (1996) recommendations, and Cd concentrations in soil were also above acceptable limits. The study concluded that contaminated irrigation water, especially wastewater, was the primary source of heavy metal accumulation in vegetables. These findings support the results of this study, which similarly identified wastewater irrigation as the main source of vegetable contamination, rendering these crops unsuitable for human consumption. Furthermore, Ismail *et al*. (2014) found that vegetables irrigated with canal water contained higher heavy metal concentrations compared to those irrigated with tubewell water, corroborating this study's conclusions.

The Pakistan Council of Research in Water Resources (PCRWR, 2006) conducted a study in Faisalabad, Pakistan, to evaluate the impact of industrial and sewage effluents on vegetables. The research indicated that vegetables irrigated with the wastewater from industrial area were significantly more contaminated with heavy metals as compared to grown with sewage water. Industrial emissions containing elevated levels of chromium, cadmium, nickel, manganese, lead, and zinc exceeded permissible limits and entered the food chain, making the vegetables toxic to both plants and humans. These findings are consistent with this study's conclusion, emphasizing that untreated wastewater poses a serious health risk to the population.

Iqbal *et al*. (2019) reported that vegetables cultivated in soils irrigated with wastewater contained heavy metal concentrations exceeding permissible limits. Regular consumption of these vegetables can lead to the accumulation of harmful metals such as Pb, Cu, Zn, and Fe in the human body. Similarly, Ahmad *et al*. (2016) observed that leafy vegetables like cabbage, cauliflower, and spinach thrive when irrigated with sewage water, whereas root vegetables such as carrots and radishes are more sensitive to wastewater. These findings reaffirm that vegetables grown using untreated industrial wastewater pose significant health risks due to heavy metal accumulation.

Numerous studies, including those conducted by Khan *et al*. (2016), Raja *et al*. (2015), Singh *et al*. (2010), Qishlaqi *et al*. (2008), Perveen *et al*. (2012), and Mahmood and Malik (2014), have extensively documented the health risks associated with heavy metals in vegetables irrigated with wastewater. For instance, Mahmood and Malik (2014) identified spinach, Brassica, and coriander as posing severe health hazards due to high levels of cadmium (Cd) and manganese (Mn). These findings are consistent with this study, where elevated health risk index (HRI) values were observed, correlating with high total target hazard quotient (TTHQ) values. This underscores that irrigation with untreated wastewater leads to significant health risks, particularly for vulnerable groups such as children and adults.

Likuku and Obuseng (2015) reported elevated health risk index (HRI) values for heavy metals such as cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), lead (Pb), and zinc (Zn) in vegetables irrigated with treated wastewater. This underscores that even treated wastewater, if not properly managed, can pose significant health risks. Similarly, Balkhair and Ashraf (2016) and Hamid *et al*. (2016) observed high HRI values for Cd, Pb, and Cr in vegetables grown with wastewater irrigation. These findings align with the research of Khan *et al*. (2015), Ahmad *et al*. (2016), and Islam *et al*. (2017), all of which highlight that vegetables which are irrigated with contaminated wastewater are a source of both carcinogenic and non-carcinogenic health risks.

The collective findings of these studies reveal several critical concerns. Heavy metals such as Cd, Pb, Cr, Mn, and Ni are persistent environmental contaminants that bioaccumulate in the edible parts of vegetables. This bioaccumulation makes dietary intake one of the primary pathways for human exposure, posing serious health risks over time. Secondly, wastewater irrigation is a major source of hazardous metals as well as providing vital nutrients for crops, especially in areas with scarce water supplies where untreated or partially treated wastewater is frequently utilized..

This study reinforces the conclusions of prior research, emphasizing the severe health hazards, including increased cancer risks, related with consuming vegetables irrigated with untreated wastewater. The findings stress the urgent need for effective wastewater treatment systems and strict monitoring of irrigation practices to minimize heavy metal contamination in food crops. Additionally, public awareness campaigns and policy interventions are critical to addressing this pressing environmental and public health issue. Expanding research to explore bio-remediation techniques and alternative irrigation methods could provide sustainable solutions to mitigate these risks in the future.

Conclusions: Certainly, here's an extended conclusion based on the provided findings:

Conclusion: This study investigated the accumulation of heavy metals (Cd, Cr, Cu, Mn, Ni, and Pb) in vegetables grown in Multan, Pakistan, using various irrigation sources, including wastewater. The results revealed significantly higher levels of heavy metals in vegetables cultivated with wastewater compared to those irrigated with canal or tubewell water.

The study further assessed the potential human health risks associated with the consumption of these vegetables. A concerning finding was that vegetables grown with wastewater irrigation posed a "carcinogenic health risk" to individuals across all age groups, from children to adults. These vegetables were deemed unsuitable for human consumption due to the elevated levels of heavy metals. In contrast, vegetables grown with canal and tubewell water were found to be safe for consumption and did not pose significant health risks.

Among the different vegetable types analyzed, leafy vegetables exhibited the highest levels of heavy metal accumulation and, consequently, the highest carcinogenic health risks. This is likely due to their high surface area and ability to readily absorb contaminants from the soil.

Multivariate statistical analysis confirmed that wastewater irrigation is a major contributing factor to the elevated levels of heavy metals in soil and vegetables. This highlights the critical need for proper treatment of wastewater before it can be used for agricultural purposes.

Recommendations: Based on the findings of this study, it is recommended that wastewater containing heavy metals should not be mixed with canal water or used directly for irrigating vegetables without undergoing proper treatment. Following recommendations are made in this regard

- **Wastewater Treatment:** Implementing effective wastewater treatment systems is crucial to remove heavy metals and other contaminants before using wastewater for irrigation.

- **Alternative Irrigation Sources:** Promoting the use of alternative irrigation sources, such as treated wastewater, rainwater harvesting, and drip irrigation, to minimize the reliance on untreated wastewater.

- **Monitoring and Surveillance**: Develop and implement a comprehensive monitoring system to regularly evaluate heavy metal concentrations in soil and vegetables grown in wastewater-irrigated areas.

- **Public Awareness**: Increase public awareness through education campaigns about the health hazards of consuming vegetables cultivated using untreated wastewater.

- **Policy Interventions**: Enforce strict regulations to prohibit the use of untreated wastewater in agriculture and promote compliance through effective oversight and penalties..

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