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Risk Assessment of Heavy Metal Accumulation in Leafy Vegetables Around Wastewater-irrigated Areas

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Abstract: The consumption of heavy metal-contaminated vegetables poses a threat to human health and the environment. This study assessed the level of heavy metals in selected leafy vegetables collected from wastewater-irrigated agricultural land located at Jalkuri Union of Siddhirganj Upazila in Narayanganj district of Bangladesh. The mean concentrations of metals were decreasing in the following order: Fe > Mn > Zn > Pb> Cr> Cu > Ni > Cd in wastewater, Fe> Mn > Cr > Zn > Ni > Pb> Cu> Cd in irrigated soil, and Fe > Zn > Mn> Cu> Pb > Cr> Ni > Cd in leafy vegetables. The contamination factor (*CF*) showed that the soils were moderate to highly contaminated by Cr and Cd. The pollution load index (*PLI*) and geo-accumulation index (I_{geo}) values of the analyzed samples revealed that the soils were non-polluted to moderately polluted. The target hazard quotients (*THQ*) for most of the metals were <1, suggesting non-carcinogenic health hazards for humans. The target carcinogenic risk (*TCR*) of heavy metals, except for Pb, was above the safe standard, suggesting a carcinogenic risk (*CR)* for their consumption. It is a matter of concern that regular intake of contaminated leafy vegetables in the area would increase health risk, as the hazard index (*HI*) was greater than 1. The study observed that vegetables should not be irrigated with contaminated water, and industrial wastewater must be properly treated before discharging into the environment.

Keywords: *Contamination, Heavy metals, Irrigation, Soil, Vegetables, Effluent-contaminated water*

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1. Introduction

In Bangladesh, industrial waste is being released randomly, without any environmental consideration, into open surfaces and waterbodies, including ponds, lakes, canals, and rivers. Large amounts of effluents are released by industries every day, and they are either untreated or poorly treated before being released into rivers, surface water, agricultural fields, and irrigation canals (Islam and Mostafa, 2022; Shakil and Mostafa, 2021a). The uptake of heavy metals by plants growing in contaminated irrigated water is of great concern to human health as they enter the human body through the food chain. Heavy metals, including Pb, Zn, Cd, Cr, Ni, and Cu, are usually found at higher levels in soils and waters around industrial waste dumping and effluent discharge areas in Bangladesh (Islam and Mostafa, 2021a). These metals might be taken up by the growing vegetables around effluent discharge areas (Rahim and Mostafa, 2021). Although the practice of using wastewater in agriculture is common, heavy metals deposit on soils or sludge, posing threats to crops and vegetables (Parvez et al., 2023; Khan et al.,2019; Chang et al., 1984). It is important to examine these crops and vegetables to ensure a safe limit for human consumption at international standards (Saha et al., 2021; Shakil and Mostafa, 2021b; Redwan and Salama, 2006). A large portion of the population benefits from knowing how to include vegetables in their daily diet. On the other hand, due to a lack of scientific knowledge and the cultivation of land, some people use abundant resources such as wastewater, including sewage water, storm water, etc., which are significant sources of heavy metals in vegetables (Islam and Mostafa, 2021b and c). The absorbed metals get bioaccumulated in the roots, stems, fruits, grains, and leaves of plants (Sultana et al.,2019; Ugurlu, 2004). Some heavy metals, like Cd and Pb, are particularly hazardous to plants, animals, and humans. (Islam et al., 2022; Ahmed et al., 2019; Alloway and Jackson, 1990). Pb and Cd can easily accumulate in soil due to their low solubility and can persist in the environment for a long time (Hossen and Mostafa, 2023). This study aimed to assess the heavy metal concentrations in the soil and leafy vegetables, as well as various pollution indices, to understand the health risks associated with human consumption of the vegetables. The study area was in Jalkuri Union, Shiddhirganj Upazila, of Narayanganj district to assess the heavy metal levels of Cu, Mn, Cr, Pb, Ni, Zn, Fe, and Cd in vegetables.

2. Materials and methods

2.1. Study area

The study selected agricultural fields near the industrial zone of Jalkuri union of Siddhirganj upazila in Narayanganj district, located beside the Sitalakhya river in Bangladesh (Figure 1). The Siddhirganj industrial zone has more than 15 thousand factories and industries. A total area of 22.71 sq km of the district lies between 23o.66'424 north latitude and 90o.49'183 east longitude. Several industries, including textile and dyeing, chemical, pulp, and paper industries, discharge untreated or poorly treated effluent into the nearby canals, which flow into the Sitalakhya river. The industrial effluent discharge directly into the nearby surface water bodies severely degrades the water and sediment quality of the river (Islam et al., 2014). Agricultural fields beside the canals have been irrigated with the contaminated water for many years.

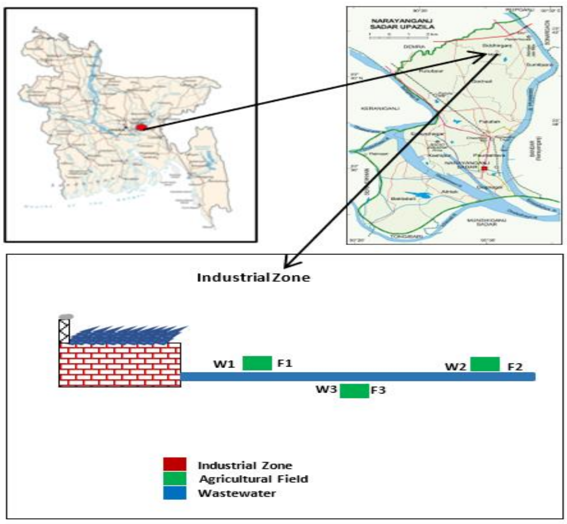

Figure 1: Sampling Location map of Study Area.

2.2. Sample collection and preparation

Different species of leafy vegetables, including *Basella alba* (malabar spinach), *Spinacia oleracea* (spinach), *Amaranthus spp* (red amaranth), *Ipomoea aquatica* (water spinach), and their growing soils and irrigated water samples, were collected from Jalkuri Union, Siddhirganj Upazila, of Narayanganj district in Bangladesh three times (pre-monsoon, monsoon, and post-monsoon) in a year between December 2021 and October 2022. These vegetables were chosen because they are the most common and popular vegetables in the area. A 95 ml water sample was taken in a beaker and mixed with 2 ml HNO3 and 3 ml HCl to make it 100 ml, which was then warmed up on a hot plate at 90°C to concentrate it into 15-20 ml. After cooling, it was filtered using Whatman 42 filter paper and made 100 ml with distilled water (Islam and Mostafa, 2022; Mastoi et al., 1997; APHA,1985). The leafy vegetables were uprooted, then divided into three pieces (root, stem, and leaves) and oven dried at 50°C. To create a uniform powder, the dry samples were crushed and filtered through a 2-mm sieve, and 0.5g of each dried vegetable and soil sample were digested at 80°C with concentrated HNO_3, H_2SO_4, and $HClO_4$ (5:1:1) until the solution became transparent. Concentrations of heavy metals in water, soil, and vegetables were analyzed using an atomic absorption spectrophotometer (AAS). All analyses were performed in triplicate.

2.3. Statistical analysis

Several data sets of heavy metals in water, soil, and vegetables were analyzed using the Pearson correlation coefficient, statistical, and computer software, including SPSS (version 20). (Gomez and Gomez, 1984).

2.4. Environmental indices

Quantification of soil pollution

The contamination of heavy metals in soil and water was assessed by determining the Contamination Factor (*CF*), Pollution Lead Index (*PLI*), Geo-accumulation Index (I_{geo}), Enrichment Factor (EF) and Potential Ecological Risk Index (*PERI*). The study assesses the pollutant indicators based on heavy metals in the control soils of the study area.

Contamination factor (*CF*) and the degree of contamination (Cd)

The computing equations for the contamination factor (*CF*) and the degree of contamination (Cd) are as follows:

$$C^i{}_f = C^i / C^i_n \quad (1)$$

$$C_d = \sum_{i=1}^{n} C^i_f \quad (2)$$

where C^i is the measured concentration of the heavy metals in soil and C^i_n is the standard pre-industrial reference level (in mg/kg): 70 for Pb, 1.0 for Cd, 90 for Cr, 50 for Cu, 175 for Zn, 68 for Ni, and 850 for Mn (Hakanson, 1980; Turekian and Wedepohl, 1961; Kabata-Pendias, 2011).

The generalized form of *mCd* is as follows (Abrahim and Parker 2008):

$$mC_d = \frac{\sum_{i=1}^{n} C^i_f}{n} \quad (3)$$

Pollution Load Index (PLI)

The following formula, based on the pollution load index (PLI) created by Tomlinson et al. in 1980, was used to determine the extent of heavy metal pollution:

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} ..... \times C_{fn})^{1/n} \quad (4)$$

Where *n* is the number of metals.

Geo-accumulation index (Igeo)
Muller (1979) introduced the equation to represent the geo-accumulation index (Igeo), which is commonly used to measure additional metal concentrations in soil:

$$Igeo = Log_2 \left[\frac{(C_n)}{1.5 \times (B_n)}\right] \quad (5)$$

Where Cn refers to the metal concentration from analysis and Bn is the geochemical background value of that metal. For the calculation of EF, CF, and Igeo, the crustal assemblage was used as the background value (Krauskopf and Bird, 1995).

Enrichment factor (EF)
According to Taylor (1964), the enrichment factor for every single metal in the sample is enumerated by dividing its concentration ratio to the normalizing element by the same ratio obtained in the chosen baseline and is commonly computed following the relationship:

$$EF = \frac{(\frac{Cn}{CFe})\ sample}{(\frac{Cn}{CFe})\ background} \quad (6)$$

In this study, iron (Fe) was chosen as the reference element for its geochemical normalization and for the following reasons:

- Its geochemistry is comparable to that of numerous trace metals.
- It is associated with fine, solid surfaces.
- Its natural concentration is typically uniform. (Bhuiyan et al., 2010)

The EF values close to unity indicate the crusted origin (comparable to those of the UCC) of the metals, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF>1 indicates that the element is of anthropogenic origin (Szefer et al., 1996).

Potential Ecological Risk Index (PERI)
The PERI quantifies the possible threat provoked by trace element toxicity and the sensitivity of the environment to the studied pollutants.

$$Er^i = T_r^i \times C_f^i \quad (7)$$

$$PERI = \sum_{i=1}^{i=n} Er^i \quad (8)$$

Here, Eir indicates the value of monomial ecological risk, and Tir value is the toxic response factor.

Bioconcentration factor (BCF)

The following formula was used to calculate the transfer of heavy metals from soil to plants:

$$BCF = \frac{C_{plant}}{C_{soil}} \quad (9)$$

Among them, C_{plant} is the concentration of heavy metals in plant parts and C_{soil} is the concentration of heavy metals in the soil.

Estimated daily intake of heavy metals (EDI)

As stated by Chen et al. (2011), use the following formula to calculate the value of the *EDI* of each heavy metal in each malabar spinach, spinach, red amaranth and water spinach:

$$EDI = \frac{EF \times ED \times FIR \times CM \times CF}{BW \times TA} \times 0.001 \quad (10)$$

EF is the exposure frequency (365 days/year), *ED* is the duration of exposure (65 years) based on the average lifespan (Woldetshadik et al., 2017), and *FIR* is the consumption of vegetables (leafy) per person 345 g/person/day for adult and 232 g/person/day for children, respectively, *CM* is the concentration of heavy metals in vegetables (mg/kg dw), *CF* is the concentration conversion factor (0.085) was used to convert fresh green vegetable weight to dry weight as subscribed by (Rattan et al., 2005; Arora et al., 2008; Harmanescu et al., 2011), while the average adult and child body weight were considered to be 55.9 and 32.7 kg (Ge, 1992; Wang et al., 2005); *TA* (averaging time) 365 days/year × number of exposure years (65 years) (Woldeshadik et al., 2017) and 0.001 is the unit conversion factor.

Target Hazard Quotients (THQs)

Accordingly, the target hazard quotient values of the populace because of the intake of infected vegetables had been calculated as the following formula (Zheng et al., 2007; Khan et al., 2008; Chen et al. 2011; Ezemonye et al., 2019):

$$THQ = \frac{EDI}{RfD} \quad (11)$$

EDI is the estimated daily intake of heavy metals in the population, in mg/day/kg body weight, and *RfD* is the oral reference dose (g/day/kg) of each heavy metal. The oral reference doses (*RfD*) of heavy metals (mg/kg/day) Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb were 1.5, 0.14, 0.7, 0.02, 0.04, 0.3, 0.003 and 0.004, respectively. (US department of health, 2008; Verma et al., 2015; USEPA,2015; Antoine et al. 2017).

hazard index (*HI*)

As suggested by Antoine et al. (2017), the *HI* of the heavy metals in this study was calculated using the following equation:

$$HI = \sum_{i=1}^{n} THQ \quad (12)$$

HI is the sum of various hazards associated with heavy metals.

Target carcinogenic risk (TCR)

The *TCR* value was calculated by the following equation:

$$TCR = EDI \times CSF \quad (13)$$

Where CSF represents the cancer slope factor of the carcinogenic elements. According to the previous report, Cd, Pb, Ni, and Cr were considered as carcinogenic elements and the *CSF* values were selected as 6.1, 0.0085, 0.84, and 0.5 mg/kg/day, respectively (Antoniadis et al., 2019).

The sampling was conducted in May 2022–December 2023 (pre-monsoon, monsoon, and post-monsoon) and collected from three agriculture fields. Four different vegetables, i.e., malabar spinach, spinach, red amaranth, and water spinach, were collected from selected agricultural fields. Specifically, these vegetables were chosen because, in the study area, only these are prevalent and grow in abundance. They grow throughout the year, making them good options to assess the year-long effect.

Table 1: Description of the selected vegetables cultivated in Jalkuri Union, Shiddhirganj Upazila of Narayanganj, Bangladesh

Common Name	Vernacular Name	Scientific Name	Family	Type of vegetables	Edible Part
Malabar Spinach	Pui Shak	*Basella alba*	Basellaceae	Leafy vegetables	Shoot (tender stem and leaves)
Spinach	Palong Shak	*Spinacia oleracea*	Amaranthaceae	Leafy vegetables	Shoot (tender stem and leaves)
Red Amaranth	Lal Shak	*Amaranthus spp*	Amaranthaceae	Leafy vegetables	Shoot (tender stem and leaves)
Water Spinach	Kalmi Shak	*Ipomoea aquatica*	Convolvulaceae	Leafy vegetables	Shoot (tender stem and leaves)

3. Results and discussion

3.1. Heavy metal contents in water

The concentration of different heavy metals in wastewater at the Narayanganj industrial area of Bangladesh is shown in Table 2. The analysis of metal concentrations was compared with the other reported wastewater discharges into surface water bodies. The mean concentrations of Cr, Mn, Fe, Ni, and Pb in wastewater exceeded the standard limit set by WHO (2011), except for the concentration of Zn. It can occur due to the flushing of the metal from immobilized deposits like domestic as well as the discharge of waste water containing metal complex dyes by the textile industry. However, according to the DoE (2023), only Pb exceeded the permissible limit. It was apprehended that the source of higher Pb content was not only industrial effluents but also geogenic sources. Long-term accumulation of Pb from motor vehicle emissions might be one of the major sources of higher Pb content in the water. In contrast, none of the metals exceeded the standard limit, according to FAO (2021). Based on the average concentrations of heavy metals, the order of heavy metal concentration in wastewater was Fe> Mn > Zn> Pb> Cr> Cu> Ni> Cd. The heavy metal concentrations of the wastewater were almost similar to those observed by Sharma et al. (2007), where Pb, Cu, Zn, Ni, Cd, and Cr were found to be 0.08–0.10, 0.04-0.11, 0.09–0.2, 0.03–0.05, 0.01-0.02, and 0.03-0.09 mg/L, respectively, at different sites in wastewater used for irrigation in the suburban region of Varanasi, India. Hasan et al. (2022) reported values in textile dyeing wastewater in Gazipur that were similar to Cr (0.329) and Fe (0.731), but higher than the present study for Ni (0.373), Cu (0.11), Zn (0.594), and Cd (0.103). Islam et al. (2022) reported that the concentration of heavy metals in the dyeing industry of Rajendrapur, Gazipur, was comparatively higher for Cr (0.24), Mn (1.60), Fe (4.28), Ni (0.44), Cu (1.04), Zn (1.97), Cd (0.28), and Pb (3.42) than in the present study. Moreover, Ahmed et al. (2019) observed in Mokesh Beel, Industrial Area, Gazipur that all metals were lower than the present study except Fe (4.08). The untreated effluent discharge from industries introduces large amounts of pollutants into surface water bodies, poses threats to aquatic life and food chains, and makes it difficult for sustainable water resource management.

Ecological implications of heavy metal contamination

In the study area of Narayanganj, industrial activities and leaching from municipal dumpsites were the main sources of metal pollution in the groundwater. Furthermore. The excessive use of fertilizers, pesticides, and chemicals (toxic heavy metals), in which pollutants migrate to groundwater and reach the water table, poses significant threats to the quality of groundwater. If these contaminants are present in the groundwater at levels higher than the permissible recommended concentration, they cause health problems throughout the food chain (Sasakova et al., 2018). Contaminated groundwater can lead to soil contamination and degradation of land quality. The soluble heavy metals can accumulate in the root zone, affecting vegetation growth, and can be bioaccumulated in human and animal tissues via the food chain (He and Li

2020). Groundwater contamination also impacts environmental quality, natural ecosystems, and long-term socioeconomic development (Li and Wu, 2019; Siddique et al., 2019).

Table 2: Seasonal mean concentration of heavy metals in water samples.

Name of Metal (mg/L)	Pre-monsoon	Monsoon	Post-monsoon	Mean±Std	Standard Limit		
					A	B	C
Cr	0.094±0.004	0.087±0.006	0.085±0.015	0.089±0.005	0.50	0.05	0.1
Mn	0.508±0.034	0.491±0.041	0.504±0.041	0.501±0.009	2.00	0.5	-
Fe	0.731±0.058	0.705±0.055	0.730±0.055	0.722±0.015	3.00	0.3	-
Ni	0.055±0.005	0.052±0.002	0.053±0.001	0.053±0.002	1.00	0.02	0.2
Cu	0.071±0.002	0.071±0.004	0.070±0.006	0.071±0.001	3.00	-	0.2
Zn	0.178±0.052	0.202±0.082	0.184±0.051	0.188±0.012	5.00	3.0	0.2
Cd	0.019±0.008	0.028±0.046	0.014±0.003	0.020±0.007	2.00	-	-
Pb	0.143±0.059	0.158±0.059	0.102±0.020	0.134±0.029	0.10	0.01	5.0

DoE, 2023[a], WHO, 2011[b], FAO (irrigated water, 2021)[c]

3.2. Heavy metal contents in soil

The variation of different heavy metals in soil at the Narayanganj industrial area, Bangladesh, is represented in Table 3. A significant amount of Cd (4.973 mg/g) in soil was found, which was higher than the standard limit, while the values of Cr, Fe, Ni, Cu, Zn, and Pb were below the standard limit (Table 3). The main source of Cd in wastewater was the discharging of waste streams from various industrial processes, such as metallurgical alloys, ceramics, metal plating, pigment works, and textile printing industries (Rahman and Islam, 2010; Rahim and Mostafa, 2021). In this study, the decreasing order of heavy metals in soil was: Fe>Mn >Cr>Zn>Ni>Pb>Cu>Cd. The mean concentrations of heavy metals in the soil were lower than those reported by Ahmed and Goni (2010). Several reports showed that metal concentrations including Ni, Cu, Cr, Cd, Pb, and Zn were found to be higher than in the soils in the study areas (Ratul et.al., 2018; Rahman et. al., 2014; Goni et. al., 2014). Parvez et. al., (2023) reported some metals to have higher concentrations and others to have lower concentrations. The concentration of heavy metals in soils depends on both geogenic and anthropogenic sources. However, the concentrations of the metals were higher in industrial discharge areas, indicating geogenic sources (Islam and Mostafa, 2022). Heavy metals in the soil result in changes in soil quality and fertility, groundwater contamination, biomagnification, and ultimately irreparable damage to soil biota (Gujre, et al., 2020). Heavy metal contamination in the soil inhibits enzymatic activity and causes the attenuation of soil organic matter (SOM) and the nutrient cycle (Bakshi et al., 2018).

Table 3: Seasonal mean concentration of heavy metals in soil samples.

Name of Metal (mg/kg)	Pre-monsoon	Monsoon	Post-monsoon	Mean±Std	Standard Limit		
					a	b	C
Cr	78.00±23.3	86.00±13.2	78.00±25.2	80.667±4.6	150	90	-
Mn	310.53±99.3	309.89±103.2	307.33±99.4	309.250±1.7	-	-	-
Fe	3482.67±1551.5	3723.48±923.6	3503.33±1207.9	3569.827±133.5	-	-	-
Ni	33.08±8.2	35.85±8.5	33.34±6.0	34.090±1.5	75	40	75-150
Cu	20.31±7.9	20.85±8.6	20.47±8.0	20.543±0.3	140	35	135-270
Zn	76.46±31.4	77.86±36.2	73.64±38.6	52.653±40.1	300	100	300-600
Cd	4.95±2.9	4.98±2.9	4.99±2.9	4.973±0.02	3	0.20	3-6
Pb	31.34±9.5	30.69±9.4	30.09±9.6	30.707±0.6	300	35	250-500

EU, 2002[a], National Environmental Protection Agency of China, GB15618 (1995) (agricultural soil)[b], International guidelines for waste water irrigated soil (mg/kg) (India), Awashthi, 2000[c]

3.3. Heavy metal contents in leafy vegetables

The heavy metal concentrations in edible parts of leafy vegetables grown on agricultural land irrigated with industrial discharge wastewater in Jalkuri Union, Narayanganj, Bangladesh, are shown in Table 4. The variations in heavy metal concentrations in leafy vegetables may be ascribed to the differences in their morphology and physiology for heavy metal uptake, exclusion, accumulation, and retention (Singh et al., 2010). Table 4 shows that the concentration of Cr, Cd, and Pb in leafy vegetables was higher than the permissible limit, which may be due to industrial discharge effluent. Besides, the application of organic and inorganic fertilizers, fungicides, pesticides, manure, and biosolids in relevant fields may further contribute to increasing the level of these heavy metals (Shaheen et al., 2016; Islam et al., 2018). The higher concentration of heavy metals in leafy vegetables may be due to leaves being the main part responsible for photosynthesis, as they carry mass flow during strong transpiration. Malabar spinach, spinach, red amaranth, and water spinach are dwarfish plants with leaves closer to the ground, so the leaves were easily exposed to the soil, which may be contaminated with heavy metals (Tasrina et al., 2015). Abnormalities in plant metabolism, morpho-physiological features, plant growth, and productivity can be directly related to Pb (Tang et al., 2017). Cd causes abnormalities in different parts of the plant, such as roots, shoots, leaves, and fruits, as well as increasing the dry-to-fresh mass ratio (DM/FM) in all organs (Singh et al., 2020).

The concentrations of heavy metals in leafy vegetables were compared with the reference values recognized by FAO/WHO (2011) and other similar international standard institutions (Table 4). Hoque et al., (2021) reported that the concentrations of various heavy metals were 0.27, 1.44, 2.43, and 10.3, in Cd, Pd, Cu, and Zn, respectively, in Malabar spinach, and 0.26, 2.17, 1.25, and 11.76, in red amaranth, which were lower than the present study. Ratul et al., (2018) observed Cu (7.05), Ni (2.65), and Zn (21.096) in Malabar spinach, which was higher, and Cu (3.45), Ni (1.55), Cd (0.116), Cr (1.1), Pb (2.667), and Zn (20.674 mg/kg) in spinach, which was lower than the present study. Sultana et al. (2019) showed Cr (9.33), Ni (4.17), Cu (8.17), Zn (73.92), and Cd (2.25), in Malabar spinach, which was higher than the present study. Bigdeli and Seilsepour (2008) reported Mn (61.05), Fe (509.40), Cu (22.74), and Zn (297.40) in spinach, which was higher, while Islam and Hoque (2014) reported Cr (2.13), Ni (5.76), Cu (19.35), and Pb (1.99) in red amaranth, which was lower than the present study. Furthermore, Ahmed et al. (2019) reported in red amaranth Cr (20.04), Mn (57.91), Fe (1615.71), Ni (9.29), Cu (23.27), Zn (818.35), and Pb (497.99), which was significantly higher than the present study.

Table 4: Mean concentration of heavy metals in leafy vegetables grown in and around irrigated area of Narayanganj

Leafy vegetables	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
	Metal concentration (mg/kg)							
Malabar Spinach	4.74±0.79	29.60±9.03	223.08±84.3	1.67±0.4	6.49±1.0	20.14±4.0	1.41±0.34	4.80±1.26
Spinach	3.27±1.47	18.35±1.74	386.57±150.1	3.59±1.1	9.12±3.6	31.67±8.6	0.56±0.28	8.68±1.90
Red Amaranth	5.05±0.94	13.72±1.43	787.96±92.4	5.88±1.7	15.31±2.5	94.85±23.3	0.96±0.24	6.85±2.19
Water Spinach	5.27±2.98	21.58±9.29	391.41±135.8	5.82±1.0	10.95±3.5	26.21±9.1	1.02±0.83	5.39±1.60
FAO/WHO (2007,2011)	2.3	500	450	2.70	10	50	0.2	0.3
Codex Alimentarius Commission, 1984(Joint FAO/WHO)	5	-	425	20	40	60	0.3	5
SEPA, 2005	0.5	-	-	10	20	100	0.2	9

Table 5: Contamination factor (*CF*), Degree of Contamination (*Cd*), Modified degree of contamination *(mCd*), Pollution Load index (*PLI*) and Potential Ecological Risk Index (*PERI*) of soil samples

Sample ID	***Contamination Factor***								***Degree of Contamination***	***Modified Degree of Contamination***	***Pollution Load Index***
	Cr	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**			
SS01	0.66	0.239	0.044	0.36	0.23	0.21	1.73	0.29	3.768 (Low, $C_d<8$)	0.471 (Nil to very low $mC_d<1.5$)	0.297 (non-polluted $0<PLI\leq1$)
SS02	0.92	0.38	0.078	0.50	0.46	0.5	5.96	0.47	9.263 (Moderate $8\leq C_d<16$)	1.158 (Low $1.5\leq mC_d<2$)	1.285 (unpolluted - moderately polluted, $1<PLI\leq2$)
SS03	1.170	0.476	0.092	0.582	0.545	0.596	21.73	0.557	25.685 (Considerable, $16\leq C_d<32$)	3.211 (Moderate $2\leq mC_d<4$)	0.759 (non-polluted, $0<PLI\leq1$)

Sample ID	*Ecological Risk Index (E_r)*								*PERI*(RI)= ∑Er	Contamination Status
SS01	1.33	0.24	0.22	1.82	1.15	0.21	51.9	1.46	58.31 (Low)	*PERI*<95: Low ecological risk
SS02	1.84	0.38	0.039	2.52	2.30	0.50	178.8	2.34	189.06 (Moderate)	95<*PERI*<190: moderate ecological risk
SS03	2.21	0.48	0.46	2.91	2.73	0.60	651.9	2.79	664.1 (Very High)	190<*PERI*<380: considerable ecological risk *PERI*>380: very high ecological risk. (Hakanson,1980)

Most of the elements show a contamination factor less than 1, while Cr (SS03) and Cd (SS01, SS02, and SS03) show more than 1 (Table 5). An overall assessment showed that the contamination status for Cd (SS03) was very high (*CF*>6), which may be due to its high abundance in the environment as well as the industrial discharge effluent. The contamination status for Cd (SS01) and Cr (SS03) was within a moderate level (1<*CF*<3), whereas Cd (SS02) showed considerable contamination (3 *CF*<6). Cd and its compounds can move through the soil, but their portability depends on several factors including soil pH and the amount of organic matter, which depends on the local environment. As Cd binds tightly to organic material, it becomes immobile in the soil, gets absorbed by plants, and eventually enters the food chain (Karaca et al., 2010).

The Cd values of all the heavy metals ranged from 3.768 to 25.685 (considerably low), and the *mCd* values ranged from 0.471 to 3.211 (nil to very low-moderate contamination), with Cd having the highest impact on the overall soil quality (Table 5). The overall toxicity quality status of the soil samples was assessed by the pollution load index (*PLI*). The calculated values of *PLI* revealed that most of the samples (SS01 and SS03) were non-polluted (*PLI*<1), except for SS02, which was unpolluted to moderately polluted (*PLI*>1). A moderately high *PLI* (SS02) value might be due to the effects of anthropogenic activities (especially industrial activities) as well as less rainfall, which compromises irrigation water, leading to the absorption of heavy metals by soil. Suresh et al. (2012) illustrated that the *PLI* status provides valuable evidence to researchers and decision-makers about pollution levels in soils.

The toxic response factor Tr values are 30, 5, 2, 1, 5, 5, and 1, respectively, for Cd, Pb, Cr, Zn, Ni, Cu, and Mn (Hakanson, 1980; Xu et al., 2008). The range of ecological risk factors, Eir values, were measured using the toxic response factors, Tir values, which are 30, 5, 2, 1, 5, 5, and 1, respectively, for Cd, Pb, Cr, Zn, Ni, Cu, and Mn (Hakanson, 1980; Xu et al., 2008). The Eir values were found to be the minimum for Zn (0.208) and the maximum for Cd (651.90), and the risk factor was in the order Cd>Ni>Pb>Cu>Cr>Zn>Mn>Fe. Also, in the case of the sampling site, the PERI was recorded as SS03> SS02>SS01. The summation, E_r values (*PERI)* for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb in SS01 were lower than 95 (the minimum grade of ecological risk), indicating that the sample poses a lower potential ecological risk in this study area, whereas SS02 and SS03 showed higher *PERI* values of 189.058 and 664.066, which indicated moderate and very high ecological risk, respectively. According to the report of Islam et al., (2017), *PERI* signified the sensitivity of different biological communities to various toxic substances and showed potential ecological risk for heavy metals in the soils of the areas (Ashraf et al., 2021). So, it can be said that the presence of varied heavy metals made the study areas susceptible to ecological risk ranging from low to very high. These findings anticipated that continuous application of untreated wastewater for a long time is causing high soil contamination with trace elements in the study area, resulting in ecological risk and a contaminated food chain.

The enrichment factor (*EF*) is a widely used statistic for measuring how much the amount of an element in a sampling medium has risen due to human activity relative to normal natural abundance. The *EF* for the effluent-contaminated crop field soil was found in the order Cd>Cr>Ni>Pb>Zn>Cu>Md>Fe. The *EF* was the maximum for Cd and the minimum for Fe, as shown in Table 6. Rayhan et al., (2019) reported a higher value for Cu, Zn, and Pb than the present study. The results of the *EF* for Fe showed slight contamination, while those for Cr, Mn, Ni, Cu, Zn, and Pb showed severe contamination, and further, Cd showed high contamination in soils. The *EF* values ranging from 0.05 to 1.5 reveal a natural process that the metals supply was entirely from the crustal materials, whereas values greater than 1.5 indicated that the metals were mostly of anthropogenic origin (Zhang, 2002; Liu, 2021). The metal *EF* less than 1.5 suggested that these metals did not contaminate the soils in the studied area and that their slight accumulation is entirely natural in origin.

Table 6: Enrichment factor (*EF*) and Geo-accumulation index (I_{geo}) of soil samples

Metals	***EF***		I_{geo}	
Cr	12.56	severely contaminated	-0.74	Unpolluted
Mn	5.10	“	-2.04	“

Fe	1.00	slightly contaminated	-4.39	"
Ni	6.77	severely contaminated	-1.64	"
Cu	5.80	"	-1.87	"
Zn	6.09	"	-1.79	"
Cd	412.00	highly contaminated	4.29	extremely polluted
Pb	6.14	severely contaminated	-1.77	Unpolluted
Contamination Status	1-2 slightly contaminated 2-5 moderately contaminated 5-20 severely contaminated 20-40 highly contaminated (Birch, 2008)		$I_{geo} \leq 0$: unpolluted $0 \leq I_{geo} \leq 1$: unpolluted-moderately polluted $1 \leq I_{geo} \leq 3$: moderately polluted $3 \leq I_{geo} \leq 4$: moderately-heavily polluted $4 \leq I_{geo} \leq 5$: extremely polluted $I_{geo} > 5$: extremely polluted. (Muller G., 1979)	

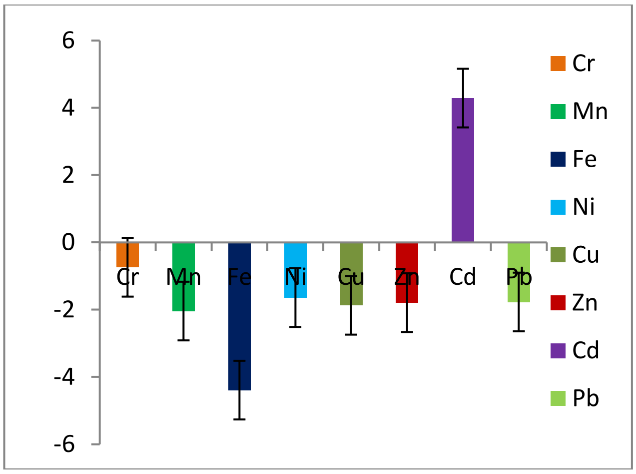

Figure 2: Geo-accumulation Index

Typically, the geo-accumulation index (I_{geo}) measures the heavy metal contamination status of soil. In this study area, I_{geo} values ranged from -0.74 for Cr to 4.29 for Cd. All elements except Cd showed negative values of I_{geo} (Table 6). The I_{geo} contamination status indicated that the area was unpolluted due to the low levels of metals in soils with all elements except for Cd. The I_{geo} mean values for heavy metals followed the order: Cd > Cr > Ni > Pb > Zn > Cu > Mn > Fe (Figure 2). The heavy metals in the soil cause changes in soil quality and fertility, groundwater contamination, biomagnification, and ultimately irreparable damage to soil biota (Gujre et al., 2020). The characteristics of lower I_{geo} values show the dilution effect of rainfall (in irrigation water) on the soil's low absorption of heavy metals. The high I_{geo} values demonstrated that the source of Cd was not natural, it would be anthropogenic as agricultural lands in the areas were irrigated with industrial discharge wastewater. The study observed that I_{geo} values for most of the heavy metals did not pollute the soil samples except for Cd, for which the soils in the areas were extremely polluted.

3.4. Bioconcentration factor (*BCF*)

The variations in heavy metal concentrations in vegetables were due to their absorption and accumulation tendencies. In all the vegetables grown in wastewater-irrigated soil, *BCF* values for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb were less than 1 (one), showing that the plants only absorbed heavy metals, but no accumulation occurred. Whereas the values for Zn in red amaranth above one (1) showed a higher potential for accumulation from the soil to vegetables. The *BCF* values for these vegetables were in the following order: Zn > Pb> Cu > Mn> Fe >Cr> Ni > Cd for Malabar spinach, Zn > Cu > Pb> Fe> Ni > Mn > Cr > Cd for spinach, Zn> Cu> Pb > Fe> Ni > Cr > Mn >Cd for red amaranth, and Cu> Zn >Ni> Pb > Fe > Mn > Cr > Cd for water spinach grown in wastewater irrigated soils (Table 7).

Table 7: Bioconcentration factor (*BCF*) of leafy vegetables

Parameter	Samples Name	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	Risk Value	Reference
BCF *(Bio-concentration factor)*	Malabar Spinach	0.063	0.089	0.063	0.051	0.308	0.257	0.050	0.157	*BCF*<1 Plants only absorb heavy metals	Ma *et al.*, 2001
	Spinach	0.042	0.06	0.107	0.103	0.396	0.403	0.017	0.291		
	Red Amaranth	0.065	0.044	0.226	0.170	0.735	1.225	0.032	0.216		
	Water Spinach	0.056	0.066	0.113	0.192	0.503	0.343	0.032	0.187	*BCF*>1 Plants absorb and accumulate heavy metals	

3.5. Health risk assessment

Several human health effects may be observed owing to heavy metal toxicity. The carcinogenic and non-carcinogenic health risks were assessed based on equations (6-9), and the results of *EDI*, *THQ*, and *TTHQ* are presented in Figure 3, 4, and 5. The analysis results showed that the *EDI* values in all leafy vegetables were lower than the provisional maximum tolerable daily intake (PMTDI) (Cr 0.2, Mn 5, Fe 17, Ni 0.3, Cu 2.0, Zn 20, Cd 0.046, and Pb 0.21) (FAO/WHO, 2011, NIN, 2009, and NRCS, 1989). For this reason, it can be said that in this study, none of the metals indicated any health risk. The estimated *EDI* through the consumption of vegetables for adults and children is shown in Figure 3, which was calculated to averagely estimate the daily metal loading into the body system of a specified body weight of a consumer (Jena et al. 2012). It may be a realistic estimate for the average intake of metals from vegetables. The *EDI* for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb did not exceed the PMTDI. The trend of metal intake from all vegetables is likely to be in the following order: Fe>Zn>Mn>Cu>Pb>Cr>Ni>Cd for both adults and children. The *EDI* values suggested that the consumption of vegetables grown in wastewater irrigated soil is nearly free of risks, as the oral reference doses (RfD) for Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb are 1.5, 0.14, 0.7, 0.02, 0.04, 0.3, 0.003, and 0.004 mg/kg/day, respectively (USEPA, 2015).

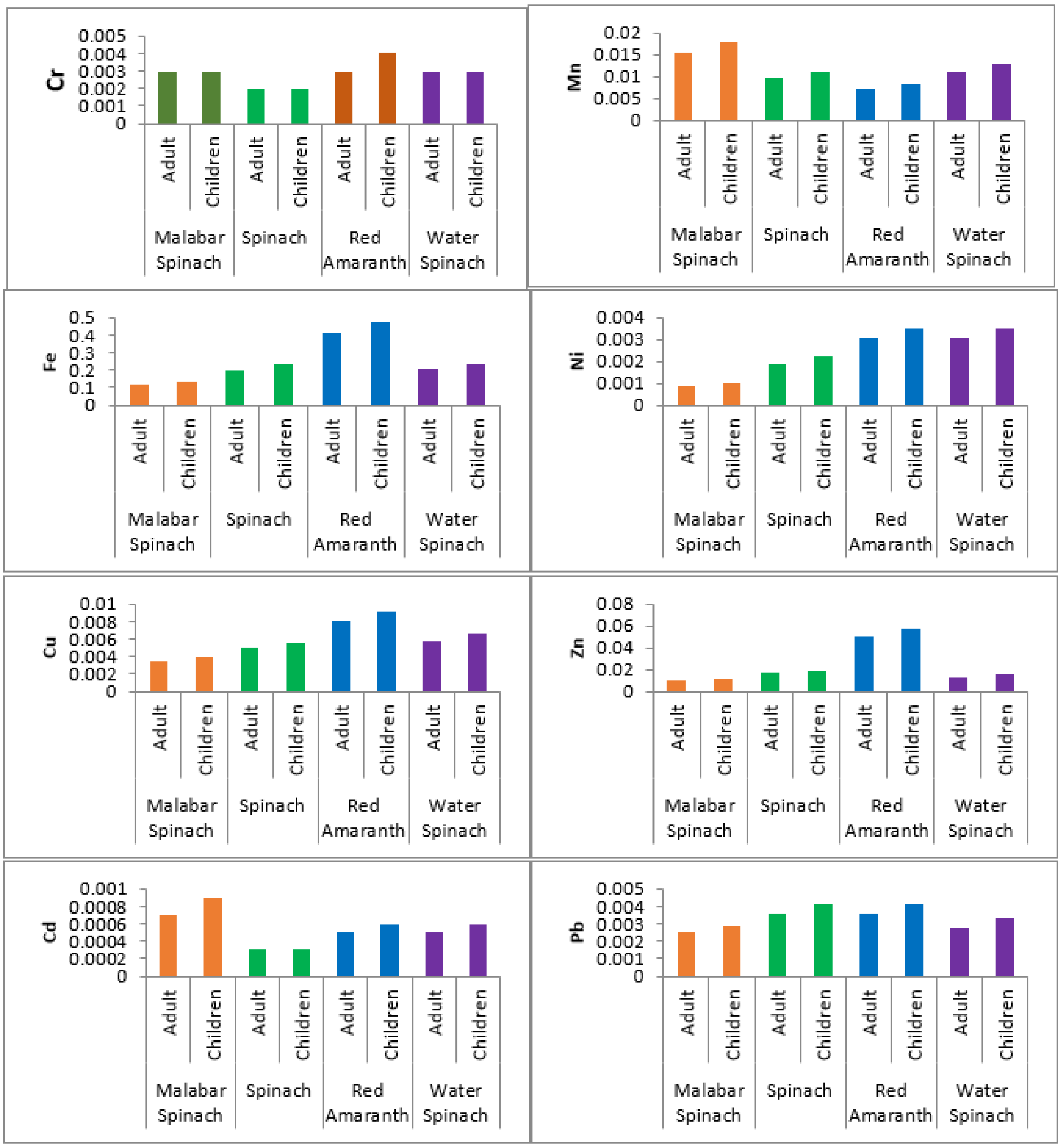

Figure 3: Estimated daily intake of metal (EDI) in leafy vegetables(mg/person/day).

The THQ is a measure of the possibility of developing non-carcinogenic health problems, and the acceptable guideline value for the *THQ* is ≤ 1.0 (USEPA, 2015). In this study, the *THQ* values of most of the heavy metals in all leafy vegetables (except Pb) were lower than the permissible limit of 1.0 for both adults and children, as shown in Figure 4. But in the case of Pb, spinach and red amaranth showed higher concentrations than the permissible limit for children. The trend of health risks for heavy metals because of the consumption of leafy vegetables was Pb > Fe > Cd > Cu > Ni > Zn > Mn > Cr. The results showed that Pb was the main metal causative of the significant health hazard, with Fe, Cd, Cu, Ni, Zn, and Mn being secondary and Cr being the least important metal. Therefore, the *THQ* analysis suggested that Pb might pose a non-carcinogenic health risk to the inhabitants of this area.

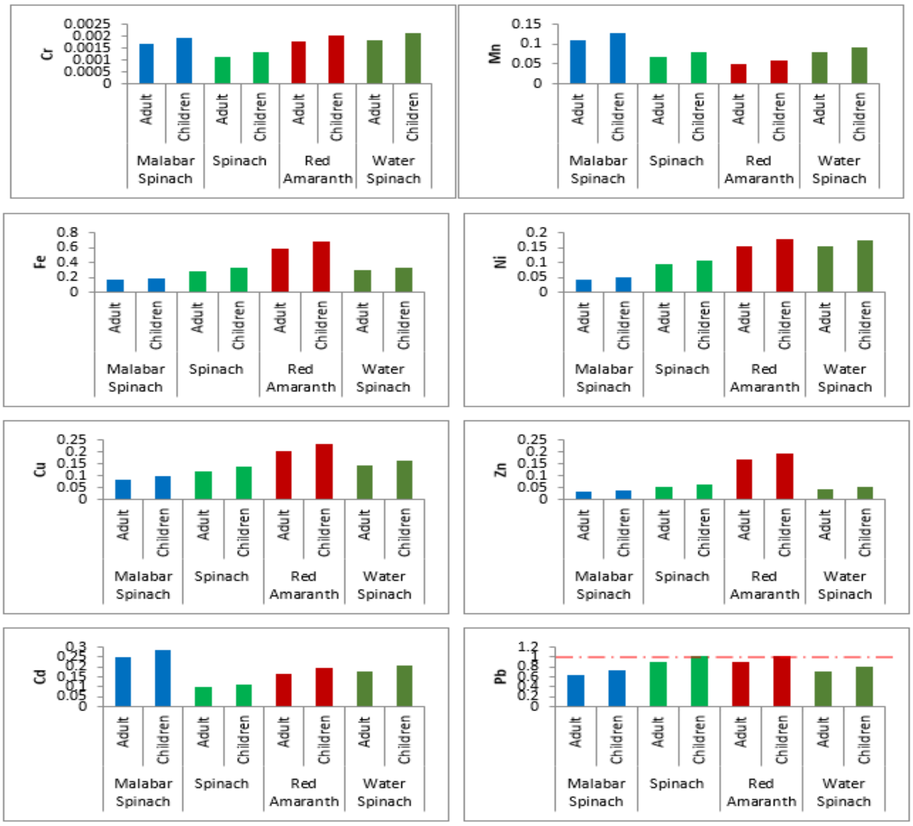

Figure 4: Target Hazard Quotient (THQ) in leafy vegetables

The hazard index (*HI*) analysis showed that the combined health risk for consumption of multiple heavy metals (Figure 5). The *HI* of metals of all the analyzed vegetables showed following descending order: red amaranth > spinach > water spinach > malabar spinach (Figure 5). Furthermore, the combined impact of all studied metals (*HI*) was higher than the acceptable limit (1.0) for all type of leafy vegetables. Therefore, intake of these sampled leafy vegetables on a regular basis is a matter of concern for non-carcinogenic health risks. According to Antoine et al., 2017 and Lie et al., 2018, value of *HI* > 10 warns of serious chronic health effects.

The *TCR* value denotes not only an estimation of expected cancer but also the probability of developing carcinogenic risk in humans (NYSDOH, 2007). In this study, the possibility of developing cancer was calculated based on the Antoniadis et al., (2019) deterministic approach. Long-term exposure to a specific carcinogen may cause cancer and health risks. The study showed the *TCR* value for Pb in all types of leafy vegetables to be acceptable, whereas Cr, Ni, and Cd posed an eminent cancer risk to the population (both adults and children) of Jalkuri Union, Siddhirganj upazila, Narayanganj, Bangladesh (Table 8).

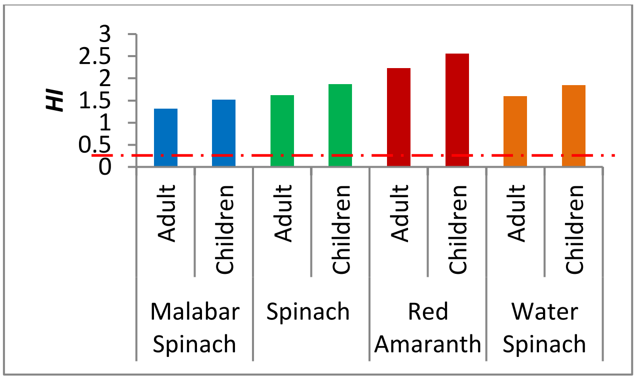

Figure 5: Hazard index (*HI*) of leafy vegetables

Table 8: Target Cancer Risk (*TCR*) of leafy vegetables

Sample Id	Individuals	Cr	Ni	Cd	Pb	*TCR* value
Malabar spinach	Adult	0.001244	0.0007308	0.0045079	0.000021403	*CR*< 0.000001 Negligible
	Children	0.001429	0.0008459	0.0051868	0.000024608	0.000001to 0.0001Acceptable
						CR> 0.0001 Risk is more
Spinach	Adult	0.000858	0.0015817	0.0017916	0.000030541	Eminent
	Children	0.000986	0.0018182	0.0020563	0.000035113	(Antoniadis *et al.*, 2019)
Red Amaranth	Adult	0.001325	0.0025911	0.0030720	0.000030545	
	Children	0.001523	0.0029786	0.0035315	0.000035113	
Water spinach	Adult	0.001382	0.0025646	0.0032640	0.000024034	
	Children	0.001589	0.0029480	0.0037522	0.000027630	

Prolonged consumption of higher concentrations of Cr in leafy vegetables creates toxicity, which causes hepatitis, gastritis, ulcers, and lung cancer (Pervin et al., 2014). Pb, a serious cumulative body poison that enters the body system through food and vegetables, affects human health and creates toxicity that can result in nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anemia, irritability, mood disturbances, coordination loss, and neurological effects (Ansari et al., 2004; Bigdeli and Seilsepour, 2008), as well as autoimmune disorders such as rheumatoid arthritis, kidney diseases, etc. (Chisti, 2018).

3.6. Pearson correlation coefficient for water, soil and vegetables

Pearson's correlation is necessary to determine the spatial and temporary relationship between the concentrations of heavy metals in the soil during different seasons and at different sampling stations. Thus, the concentrations of heavy metals were differentially correlated with the concentrations of individual heavy metals (Table 9). The table shows three different correlations, namely, very strong, strong, and moderate, were found among different heavy metals in water, soils, and vegetables, indicating that their potential originated from a common source, i.e., anthropogenic in the study area. Table 9 shows a positive correlation between Cr with Fe, Ni, Cu, Mn, Cd, and Pb, which indicates that they have a similar source and serious health hazards when they enter the human body (Ahmed et al., 2021). A strong correlation between Mn and Ni, Fe, Cu, Zn, Cd, and Zn and Ni, Cu, Mn, Cd, and Pb indicates that Mn, Fe, Ni, Cu, Zn, Cd, and Pb were controlled by identical factors such as anthropogenic activities, industrial pollution, agricultural activities, and so forth (Hanson et al., 1993; Alagarsamy, 2006; Tariq et al., 2008). A majority of elements exhibit a very poor or negative correlation, which indicates different geochemical behaviors and external input operating (Ray et al., 2006; Lee et al., 2021). The study suggests that water samples showed significant positive correlations with all metals, except for Ni. On the other hand, the concentrations of heavy metals in soil samples showed that all metals were strongly positively correlated with each other during the three seasons. Similarly, in vegetables, a close relationship was noted among Ni, Cu, Zn (P=0.05), and Cu-Zn(P=0.05), as well as Cr, Cd, and Mn. The remaining concentrations of heavy metals were weakly positive-negatively correlated with each other (Table 9).

Table 9 Pearson Correlation of water, soil and vegetable

Metals	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Cr	1	0.327	0.997*	0.996	0.958	0.755	0.277	-0.023
Mn	0.512	1	0.253	0.246	0.041	0.867	-0.817	0.937
Fe	0.338	0.981	1	0.999**	0.977	0.701	0.351	-0.100
Ni	0.854	0.884	0.778	1	0.979	0.696	0.358	-0.108
Cu	0.672	-0.292	-0.470	0.189	1	0.533	0.543	-0.310
Zn	-0.525	-0.999**	-0.978	-0.891	0.277	1	-0.421	0.638
Cd	0.050	-0.833	-0.923	-0.477	0.773	0.824	1	-0.967
Pb	-0.820	-0.911	-0.815	-0.998*	-0.127	0.918	0.531	1
Cr	1							
Mn	0.433*	1						
Fe	0.374*	-0.357*	1					
Ni	0.433*	-0.339	0.718**	1				
Cu	0.436*	-0.278	0.842**	0.794**	1			
Zn	0.257	-0.409*	0.906**	0.620**	0.824**	1		
Cd	0.613**	0.593**	-0.018	-0.003	0.144	0.010	1	
Pb	0.287	-0.022	0.490**	0.431*	0.471**	0.448**	-0.017	1

4. Conclusion

The analysis results showed that the mean concentration of metals was decreasing in the following order: Fe > Mn > Zn > Pb> Cr> Cu > Ni > Cd in wastewater, Fe> Mn > Cr > Zn > Ni > Pb> Cu> Cd in irrigated soil, and Fe > Zn > Mn> Cu> Pb > Cr> Ni > Cd in leafy vegetables. This study observed that the contamination factor (*CF)* of Cr and Cd for samples (SS02 and SS03) was higher than one, indicating that the areas were moderate to highly contaminated with these heavy metals. However, the pollution load index (*PLI*) values indicated the area was to be non-polluted to moderately-polluted. The geo-accumulation index (I_{geo}) values further strengthen the indications that the area was being unpolluted except for Cd, as all elements have negative values, while the Cd value suggested heavy and extreme pollution. The target carcinogenic risk (*TCR*) of heavy metals, except for Pb, was above the safe standard, suggesting a carcinogenic risk (*CR*) for their consumption. It's a matter of concern that regular intake of contaminated leafy vegetables from that area would increase health risk, as the total target hazard quotient (*TTHQ*) was greater than one. Therefore, regular monitoring, effective steps, and emergency initiatives should be taken to ensure the safe consumption of vegetables in the area. Continuous polluted water irrigation has led to an increase in heavy metal contents in agricultural soil and leafy vegetables, which finally affects health through the food chain. The study observed that vegetables should not be irrigated with contaminated water, and industrial wastewater must be properly treated before discharging into the environment. The government and non-government organizations have to take a closer look at areas where agricultural lands are irrigated with industrial discharge contaminated water, and publicity and awareness build-up programs should be taken to ensure food safety and security for achieving sustainable development goals (2, 3, 6, and 11).

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