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Spectroscopic study of Cu, Mn, Cd as heavy metals in agricultural samples

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Abstract: Heavy elements represent a source of toxicity when accumulate in the soil and be transmitted to plants, animals and humans through food chains that may affect the human and the animal health. In this study, environmental samples, vegetable samples (Cabbage, Mallow, Turnip) and soil, were collected from Qaha in Qaliubia in Egypt then subjected to investigate the availability of toxic metals such as copper, manganese and cadmium using flame atomic absorption spectroscopy (FAAS) technique. We have found Cu, Mn and Cd in cabbage with concentrations around 25.28 ±1.263 ppm, 103.83 ±5.19 ppm and 0.792 ±0.0396 ppm, respectively. The Cu, Mn and Cd concentrations in Mallow were found to be 35.26 ±1.76 ppm, 142.72 ±7.14 ppm and 1.3 ±0.0649 ppm respectively. Also, the concentrations of Cu, Mn and Cd in Turnip have achieved 29.29 ±1.45 ppm, 79.33 ±3.97 ppm and 1.99 ±0.099 ppm respectively. For soil, the concentrations of Cu, Mn and Cd were 2.4 ±0.12 ppm, 4.8 ±0.24 ppm and 1.75 ±0.088 ppm respectively. It was concluded that the pollution index values for Cu, Mn and Cd in soil were 0.024 ±1.2 ×10^{-3}, 0.01 ±5.49 ×10^{-4} and 0.58 ±0.029 respectively. The pollution index values in cabbage for Cu, Mn and Cd were 0.346 ±0.017, 15.708 ±0.785 and 3.96 ±0.198 respectively. The pollution index values for Cu, Mn and Cd in Mallow were 0.073 ±0.024, 21.59 ±1.08 and 6.5 ±0.32 respectively. The pollution index values for Cu, Mn and Cd in Turnip were 0.401 ±0.019, 12 ±0.6 and 9.95 ±0.5 respectively. The observed new results are important to monitor the environmental pollution in the studied samples which have an impact on human health.

1. Introduction

Food has been an integral part of human diet since the dawn of time; it is a rich source of enzymes, vitamins, and minerals. Modern diet, on the other hand, emphasises the importance of vegetables and fruits in improving life satisfaction [1]. Vegetables are the most polluted food [2], absorbing heavy metals and accumulating them in edible and non-edible pieces in concentrations large enough to cause health problems in humans [3, 4]. Heavy metals in high amounts harmed the immune, cardiovascular, renal, and neurological systems, as well as causing bone disorders and other health issues [5]. Heavy metals in contaminated soils have been linked to an increased risk of cancer [6, 7]. Metal pollution in some Egyptian landscapes is still widely common, resulting in environmental toxicity [1, 8].

Heavy metal pollution in soils, such as Cd, Ni, Zn, Pb, and Cu, has risen sharply in recent decades [9] as a result of mining, smelting, refining, agricultural fertilisers and pesticides, urban waste, traffic pollutants, and industrial effluents. Heavy metal pollution in soils is now common [11]. Land pollution caused by heavy metals has a significant negative impact on the climate and

ecosystem all over the world [12, 13]. Food waste is caused by heavy metals dispersing in irrigated soils and growing plants, which can be toxic to humans and animals [2]. Heavy metals in effluents are poorly absorbed in water and thus cannot be degraded; as a result, they appear to settle in soils and therefore in plants [14–18]. Heavy metals also persist in the soil, where they leach into the groundwater, where they can stimulate antioxidant enzymatic activities in plants or become adsorbed by solid soil particles [19]. Because of the continuing rise in metal quantities in the atmosphere, most developed countries' governments have changed their laws to reduce the prevalence of these elements in the environment. For instance, it is well established that lowering lead levels in gasoline has resulted in a significant reduction of this metal in the atmosphere [20–23]. Several studies have shown that children's exposure to soils can result in their ingestion of a significant number of toxic elements [24]. Furthermore, children are at higher risk than adults due to their decreased susceptibility, higher ingestion rates from the gastrointestinal tract, and unique practices (hand–mouth operation, outdoor sports, poor hygienic habits, etc.) [24, 25].

There are advanced techniques that have been used for the analysis of soils: impedance spectroscopy [26] which has been used for soil analysis [27], high sensitivity, low detection limits, wide dynamic range, and high-speed multi-element analysis, inductively coupled plasma optical emission spectrometry (ICP-OES) [28] and laser spectroscopic techniques [29–31] (like laser- induced breakdown spectroscopy (LIBS) [32–38].

Atomic Absorption Spectrometry (AAS) is a method for calculating the ingestion of compounds introduced in soil experiments by measuring the amount of radiation absorbed by the compound portion of intrigue. This is followed by an examination of the spectra produced when the sample is irradiated. It is based on the Beer-Lambert law, which uses an atomic absorption method to calculate vitality as photons of light absorbed by the sample. A detector matches the wavelengths of light emitted through the sample to the wavelengths that went through the sample initially. The change of wavelength absorbed is then integrated by a signal processor, resulting in peaks in energy absorption at discrete wavelengths in the readout [39].

This work is aimed to determine the concentrations of heavy and toxic metals such as copper, manganese and cadmium in environmental samples: vegetable samples (Cabbage, Mallow, Turnip) and soil precisely.

2. Materials and methods
2.1 *The area of study*

The studied area is located at Qaha, Al- Qaliubiya Governorate, Egypt. Qaha city located 25 km north of Cairo. It exists in the Delta's rich agriculture in the south, which is well-irrigated by canals that branch off the Delta Barrage. Qaha city is a well-known industrial city with a quit number of factories and companies such as chemical industries, batteries, war products, shoe varnishes, aluminum tubing and fireworks.

2.1.1 *Sample collection and sample preparation*

Vegetable samples (cabbage, mallow, turnip) and soil were collected in winter 2019. The soil sample was collected using a shovel and an axe at a depth of 0-30 cm. The vegetable sample

were divided into roots, stems and leaves and then washed by bi-distilled water. The samples were left to dry by air and then dried by an oven at 60℃ until the weights remain constant, ground using a mortar and pestle. After that, they were stored in vacuum bags.

The digestion method: 0.2 gm of each sample were digested in 10 ml acid mixture of HNO_3: $HClO_4$ (5:1 v/v) for 8 hours at 80℃, then the digests were filtered and diluted to 50 ml with double de-ionized water [40].
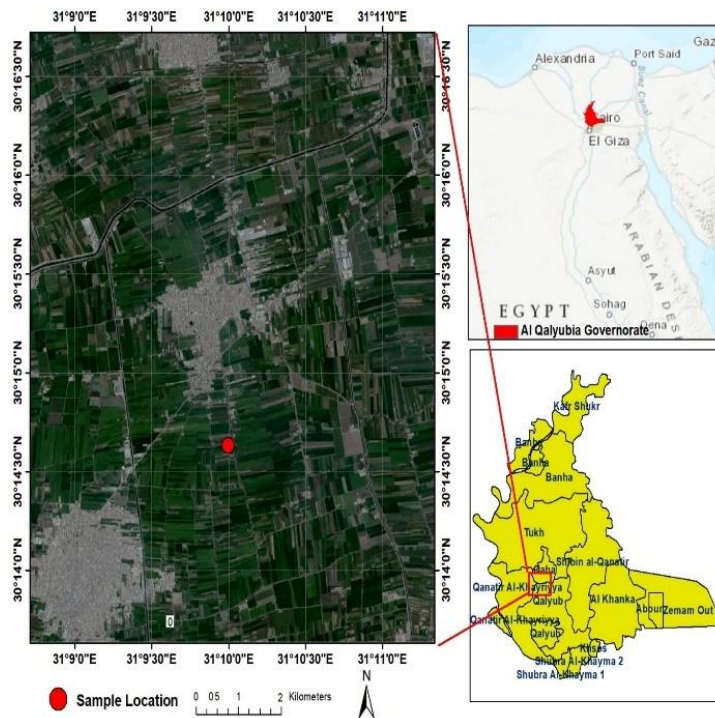

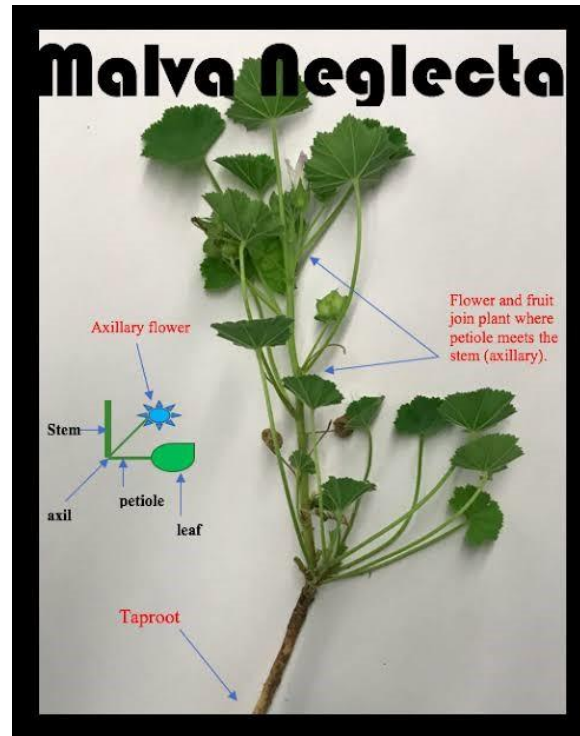**Figure 1.** The site of study

Figure 2. Cabbage

Figure 3. Mallow

Figure 4. Turnip

3. Instrumentation

The samples were analyzed using Solar S4 atomic absorption spectrometer system which installed in the faculty of women for arts, science and education, Ain Shams University, Egypt. A Quad Line deuterium lamp is used in this AA Spectrometer for background correction, which has a double beam optical system. It has an Ebert monochromatic with a resolution of 1800 lines/mm. The system allows chemical examination of various materials, mostly metals and metal alloys, after the sample has been dissolved. Nearly most of the elements (with the exclusion of non-metals) can be determined in a broad variety of concentrations using an atomic absorption spectrometer (from 0.0001 to some dozen of percentage). The system is simple to operate and provides fast, precise and repeatable analysis results. The device is easy to use and provides fast, accurate and reproducible results of the analysis. The parameter conditions of the instrument are shown in 'table 1'.

Table (1): Operating Conditions for elements measured by FAAS

Element	Wavelength (nm)	Lamp Current (mA)	Burner Height (mm)	Fuel Flow (L/min)	Band Pass (nm)	Flame Type
Cu	324.2	5	7.0	0.9	0.5	Air-Acetylene
Mn	279.5	12	7.0	1.0	0.2	Air-Acetylene
Cd	228.8	8	3.8	0.8	0.5	Air-Acetylene

Pollution index

Using a pollution index, the degree of soil pollution caused by each heavy metal was calculated (PI), calculated as:

$$PI = \frac{C_c}{C_r}$$

where C_r and C_c represent the permissible heavy metal concentration and its estimated concentration, respectively [41].

Daily Intake of Metals (DIM)

The daily intake of metals (DIM) was estimated depending on the average consummation of contaminated-plants for both children and adults. It was evaluated as [42]:

$$DIM = \frac{C_{metal} \times C_{factor} \times D_{food\ intake}}{B_{average\ weight}}$$

where C_{metal} is the heavy metal concentrations in plants (mg/kg), C_{factor} is a conversion factor, $D_{food\ intake}$ represents the daily intake of vegetables, and $B_{average\ weight}$ represents the average body

weight. A conversion factor of 0.085 was used to transform fresh green vegetable weight to dry weight [37]. The average daily intake for adults and children was assumed to be 0.345 and 0.232 kg per person per day, while the average adult and child body weights were assumed to be 55.9 and 32.7 kg [7,38]. These values were used for the calculation of HRI as well.

Health risk index (HRI)

The HRI was measured by dividing the normal consumption of metals in food by the oral reference dosage (RfD) using the following equation:

$$HRI = \frac{DIM}{RfD}$$

Oral reference doses were 0.04, 0.14 and 0.001 mg/kg/day for Cu, Mn and Cd respectively. [43]

The HRI value greater than 1 was considered as not safe for human health [44] and may pose health hazards for the consumers.

4. Results and Discussion

The amounts of heavy metals in environmental samples in Qaha are shown in 'Table 2'. From this table, the highest values of Mn concentrations in (cabbage, mallow and turnip) leaves are 119.25 ±5.96 ppm, 284.9 ±14.25 ppm and 106 ±5.3 ppm respectively. Whereas the lowest values of Mn concentrations found in cabbage stem, mallow roots and turnip roots are 87 ±4.35 ppm, 58.5 ±2.93 ppm and 53.75 ±2.69 ppm respectively. Thus, the mean values of Mn content in cabbage, mallow and turnip samples are 103.83 ±5.19 ppm, 142.72 ±7.14 ppm and 79.33 ±3.97 ppm respectively. The results of Mn content in vegetable samples are about three-folds higher than the normal level of Mn in plant 6.61 ppm 'Table 3'. This finding shows that the vegetable samples of the study area are polluted by Mn metal due to soil pollution such as pesticides and fertilizers. On other hand, the minimum concentrations of Cu in cabbage stem, mallow stem and turnip roots are 9.875 ±0.49 ppm, 16.33 ±0.82 ppm and 23.38 ±1.17 ppm respectively. The maximum concentrations of Cu in (cabbage, mallow and turnip) leaves are 46.58 ±2.33 ppm, 73 ±3.65 ppm and 32.25 ±1.61 ppm in respectively. The mean values of Cu in cabbage, mallow and turnip samples of the study area are 25.28 ±1.263 ppm, 35.26 ±1.76 ppm and 29.29 ±1.45 ppm respectively. Cu concentration in vegetable samples is about two times lower than the 73 ppm permissible value for Cu in plants 'Table 3'. This observation indicates that Cu metal has not contaminated the studied area's vegetable samples. The minimum concentrations of Cd in cabbage roots, mallow stem and turnip roots are 0.175 ±8.75×10^{-3} ppm, 0.175 ±8.75×10^{-3} ppm and 1.5 ±0.075 ppm respectively. The maximum concentrations of Cd in cabbage leaves, mallow leaves and turnip stem 2 ±0.1 ppm, 3.5 ±0.175 ppm and 2.48 ±0.124 ppm respectively. The average values of Cd in cabbage, mallow and turnip samples of the study area are 0.792 ±0.0396 ppm, 1.3 ±0.0649 ppm and 1.99 ±0.099 ppm respectively. These values are about threefold higher than the normal level of Cd in plant 0.2 ppm 'table 3'. This finding indicates that the research area's vegetable samples have been contaminated with Cd metal as a result of mining practices and a lack of environmental control.

According to 'Table 2', average Mn levels in vegetable samples from the research region are higher than Cu and Cd levels, so the levels of toxic elements in the current study's vegetable samples can be ordered in the following order: Cu > Mn > Cd. The use of chemical fertilizers and insecticides in farm fields is blamed for the contamination of radioactive metals in vegetable samples from agricultural areas.

'Table 2' shows that the soil has a high Mn content of around 4.8 ±0.24 ppm. Mn concentration of soil is about two times lower than the permissible limit of Mn in soil (437 ppm) 'Table 3'. This finding shows that the soil sample of the study area is not polluted by Mn metal. On other hand, the concentration of Cu in the soil is 2.4 ±0.12 ppm. Cu content in soil is approximately two times

smaller than the permissible level of Cu in soil of 100 ppm 'Table 3'. This result indicates that the soil sample from the research area is not contaminated with Cu metal.

Table 2: Heavy metal concentrations (Mean ± SD) in vegetable samples and soil.

Sample	Cu	Mn	Cd
Cabbage root	19.38 ±0.969	105.25 ±5.26	0.175 ±8.75× 10^{-3}
Cabbage stem	9.875 ±0.49	87 ±4.35	0.2 ±0.01
Cabbage leaf	46.58 ±2.33	119.25 ±5.96	2 ±0.1
Mallow root	16.45 ±0.82	58.5 ±2.93	0.225 ±0.011
Mallow stem	16.33 ±0.82	84.75 ±4.24	0.175 ±8.75× 10^{-3}
Mallow leaf	73 ±3.65	284.9 ±14.25	3.5 ±0.175
Turnip root	23.38 ±1.17	53.75 ±2.69	1.5 ±0.075
Turnip stem	31.25 ±1.56	78.25 ±3.91	2.48 ±0.124
Turnip leaf	32.25 ±1.61	106 ±5.3	2 ±0.1
Soil	2.4 ±0.12	4.8 ±0.24	1.75 ±0.088

'Chart 1' illustrates the concentrations of the metals (Cu, Mn and Cd) in the cabbage sample. The concentrations of Mn are about 119.25 ppm, 105.25 ppm and 87 ppm in the leaves, roots and stems, respectively. While the concentrations of Cu are 46.58 ppm, 19.38 ppm and 9.875 ppm in the leaves, roots and stems, respectively. And, finally the concentrations of Cd are 2 ppm, 0.2 ppm and 0.175 ppm in the leaves, stems and roots, respectively.

From this chart we can conclude that the concentrations of Mn, Cu and Cd increased from the roots to the leaves with high concentrations in the leaves in the cabbage sample.
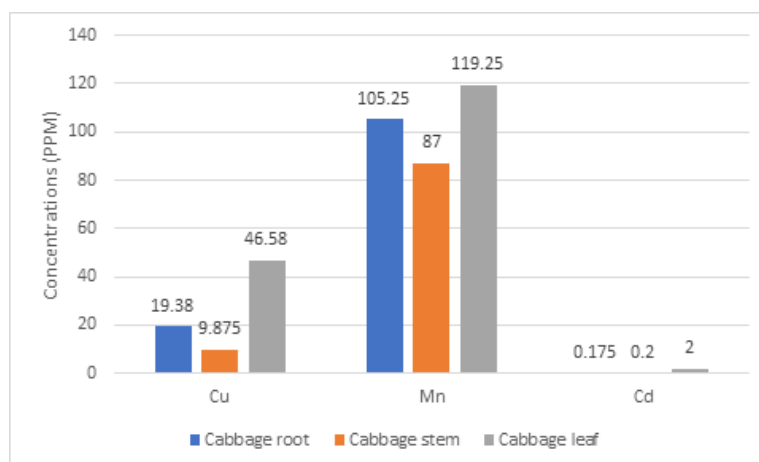

Chart 1: The concentrations of heavy metals in cabbage (root, stem, leaf)

'Chart 2' illustrates the concentrations of the metals (Cu, Mn and Cd) in the mallow sample. The concentrations of Mn are about 284.9 ppm, 84.75 ppm and 58.5 ppm in the leaves, stems and roots, respectively. While the concentrations of Cu are 73 ppm, 16.45 ppm and 16.33 ppm in the leaves, roots and stems, respectively. And, finally the concentrations of Cd are 3.5 ppm, 0.225 ppm and 0.175 ppm in the leaves, roots and stems, respectively.

From this chart we can conclude that the concentrations of Mn, Cu and Cd increased from the roots to the leaves with high concentrations in the leaves in the mallow sample.

Chart 2: The concentrations of heavy metals in Mallow (root, stem, leaf)

'Chart 3' illustrates the concentrations of the metals (Cu, Mn and Cd) in the turnip sample. The concentrations of Mn are about 106 ppm, 78.25 ppm and 53.75 ppm in the leaves, stems and roots, respectively. While the concentrations of Cu are 32.25 ppm, 31.25 ppm and 23.38 ppm in the leaves, stems and roots, respectively. And, finally the concentrations of Cd are 2.48 ppm, 2 ppm and 1.5 ppm in the stems, leaves and roots, respectively.

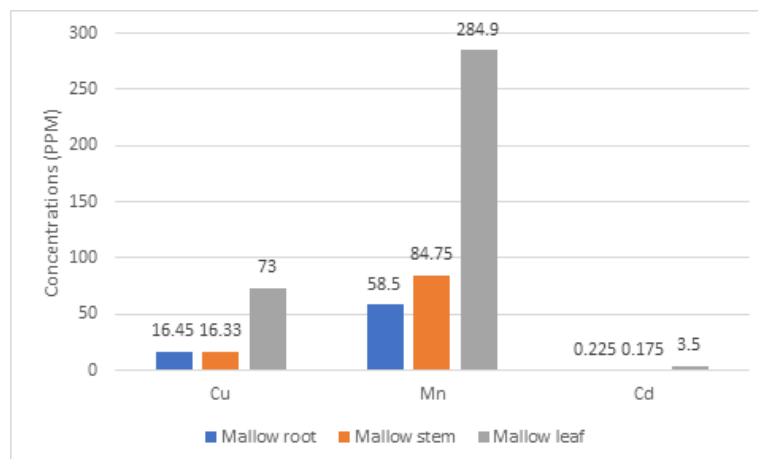From this chart we can conclude that the concentrations of Mn, Cu increased from the roots to the leaves with high concentrations in the leaves in the turnip sample. On the other hand, for Cd metal the high concentration was in the stems in the turnip sample.
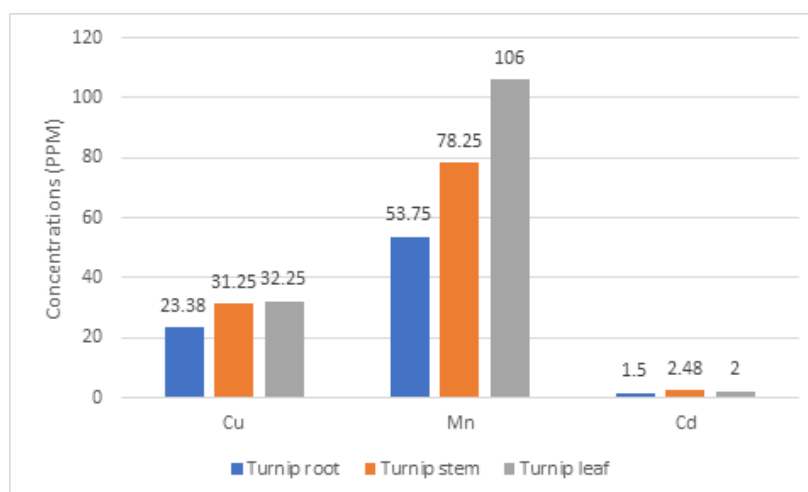

Chart 3: The concentrations of heavy elements in Turnip (root, stem, leaf)

Cd is present in the soil at a concentration of 1.75 ±0.088 ppm. This value is roughly two-thirds smaller than the appropriate Cd in soil cap of 3 ppm 'Table 3'. This finding indicates that the soil sample used in the analysis was not contaminated with Cd metal.

According to' Table 2', the average amount of Mn in the soil of the sample region is greater than the values of Cu and Cd, indicating that the toxic elements in the soil of the current study can be grouped in the following order: Mn > Cu > Cd.

'Chart 4' illustrates the concentrations of the metals (Cu, Mn and Cd) in the soil sample. The concentration of Mn is about 4.8 ppm. While the concentration of Cu is 2.4 ppm. And, finally the concentration of Cd is 1.75 ppm.

From this chart we can conclude that the soil has high concentrations of Mn, Cu and relatively low concentrations of Cd metal.
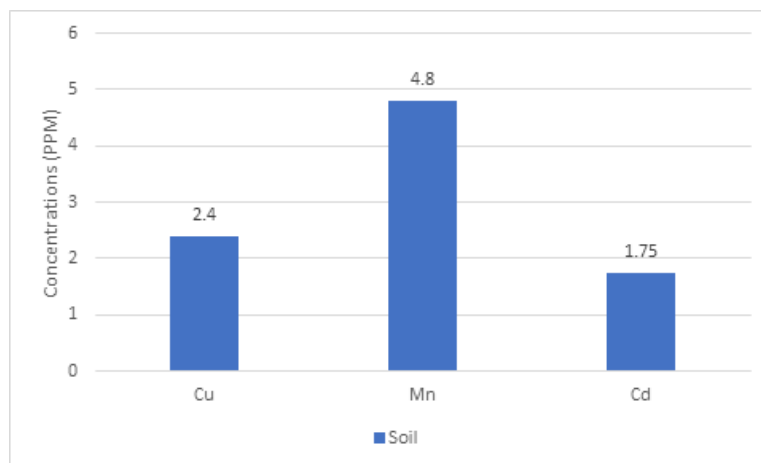

Chart 4: The concentrations of heavy metals in Soil

Table 3: Permissible concentration in agricultural systems (soil and plant) according to Food and agriculture organization (FAO)

Element	Permissible conc. In soil (ppm).[45]	Permissible conc. In plant (ppm).[46]
Cu	100	73
Mn	437	6.61
Cd	3	0.2

Pollution index

Soil is an important component of nature's dynamic structure, in which both chemical, biochemical, physical, and geological reactions occur with differing characteristics over time and space [47]. The physicochemical properties of the soil are undoubtedly influenced by the consistency of irrigation water. Irrigation of wastewater resulted in a significant improvement in soil pH and electric conductivity in the current sample. The migration, transition, and several reaction pathways of metal retention in soils are all influenced by pH, either directly or indirectly [48]. Furthermore, it is one of the most important factors affecting heavy metal mobility and adsorption in soils. Alghobar et al. (2014), in contrast to our findings, found that irrigation of waste

water lowers soil pH; this may be attributed to the high content of organic matter, which decomposes to create organic acids.

Significantly, Mn, Cu and Cd had a low concentration in soil with pollution index less than the concentrations of these metals in vegetable samples are also high. This may be due to plants' high ability to absorb and transport heavy metals from the soil to the roots 'Table 4'.

According to 'Table 5', the current study's findings showed that Mn and Cd levels in vegetable samples surpassed the safe ranges, with an emission index greater than one. Cu, on the other hand, had an emissions index of less than one.

Table 4: The pollution index values in soil

Element	Pollution index values in soil
Cu	$0.024 \pm 1.2 \times 10^{-3}$
Mn	$0.01 \pm 5.49 \times 10^{-4}$
Cd	0.58 ± 0.029

Table 5: The pollution index values in vegetable samples

Element	Pollution index values in cabbage	Pollution index values in Mallow	Pollution index values in Turnip
Cu	0.346 ± 0.017	0.073 ± 0.024	0.401 ± 0.019
Mn	15.708 ± 0.785	21.59 ± 1.08	12 ± 0.6
Cd	3.96 ± 0.198	6.5 ± 0.32	9.95 ± 0.5

Daily intake of metals

The use of plants cultivated in wastewater-irrigated soils resulted in a high daily intake of metals (DIM) 'Table 6'. The DIM of all inspected heavy metals is lower than 1 for children and adults consuming cabbage, mallow and turnip plants.

Table (6): Daily Intake of Metals (mg/day) by adults and children for individual heavy metals in vegetable samples.

Heavy metal	Cabbage		Mallow		Turnip	
	Adult	Children	Adult	Children	Adult	Children
Cu	0.01	0.015	0.018	0.02	0.015	0.018
Mn	0.05	0.063	0.075	0.086	0.042	0.048
Cd	4.16×10^{-4}	4.77×10^{-4}	6.82×10^{-4}	7.84×10^{-4}	1.04×10^{-3}	1.2×10^{-3}

Health risk assessment

The HRI is a widely used method for determining the risk of hazardous materials in foods [7]. HRIs greater than 1 are thought to be harmful to human wellbeing. Cd had an HRI greater than 1 in the turnip sample irrigated with wastewater in this analysis. Cu and Mn had HRI of less than 1 for vegetable samples irrigated with wastewater as well.

Table (7): Health Risk Index (HRI) of heavy metals for adults and children via intake of heavy metals in vegetable samples.

Heavy metal	Cabbage		Mallow		Turnip	
	Adult	Children	Adult	Children	Adult	Children
Cu	0.25	0.375	0.45	0.5	0.375	0.45
Mn	0.357	0.45	0.54	0.61	0.3	0.34
Cd	0.416	0.477	0.682	0.784	1.04	1.2

5. Conclusion

The concentrations of heavy metals in environmental samples obtained from Qaha were studied using the FAAS technique. Due to human activity, chemicals, fertilizers, industrial activities, and the lack of environmental monitoring with pollution index greater than 1, the metals Mn and Cd are most significant in the vegetable samples of the study field. The findings of the heavy metals concentrations in this analysis indicate that the vegetable samples are not contaminated by Cu, with a pollution index of less than one. Heavy metal concentrations show that the soil sample is not contaminated by Cu, Mn, or Cd, with an emission index of less than one. Children and adults consuming cabbage, mallow and turnip plants have daily intake of metals of all inspected heavy metals lower than one. Furthermore, except for Cu and Mn metals, which had HRI less than 1, the Cd heavy metal suggested a high health risk from drinking turnip plant irrigated with wastewater. The observed results are important since human health is directly impacted by consuming vegetables. Monitoring of heavy metals in vegetables needs to be continued; because these are the main sources of food for human beings in the studied area and considered as bioindicators of environmental pollution.

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