

ASSESSMENT OF HEAVY METAL CONTAMINATION IN WASTEWATER IRRIGATED FARMS IN MEKNES, MOROCCO

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(Received 11th Jan 2024; accepted 3rd May 2024)

Abstract. Wastewater is widely used for irrigation in Meknes (Morocco). It helps the farmers to cope with drought issues. However, wastewater can contain many toxic chemicals, such as heavy metals, endangering human health. This study aims to assess heavy metal accumulations in wastewater irrigated farms and to identify potential risks to human health. Sampling was conducted from urban and peri-urban farms, collecting irrigation water, soil, and a variety of irrigated vegetables (beet, cardoon, fava bean, lettuce, radish, and zucchini). Ten heavy metals were analyzed: Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The analysis was performed using inductively coupled plasma atomic emission spectroscopy. For irrigation water, all the metals were within the WHO and FAO standards except for Pb and Cr. Heavy metal pollution index indicates an acceptable overall irrigation water quality. For soil, the enrichment factor and the contamination factor show significant anthropogenic enrichment of Cd and Pb. The Metal Pollution Index and Transfer Factor reveal an elevated aptitude of metals to accumulate in beets. The assessment of health risk, using the Target Hazard Quotient and the Hazard Index, indicates potential non-carcinogenic risks related to Al and Fe in beets and lettuce consumption.

Keywords: trace metals, contamination, water quality, soil pollution, crop safety

Introduction

Wastewater irrigation is a common practice in areas affected by drought and water scarcity. This practice allows farmers to save water and nutrients. However, wastewater can contain many pollutants, such as heavy metals from industry, agriculture and domestic sources. They can be responsible for various health problems, such as gastrointestinal, renal, nervous, and immune disorders (Mamtani et al., 2011; Balali-Mood et al., 2021). Long-term exposure to heavy metals can lead to chronic diseases, organ dysfunctions, and even cancers (Jaishankar et al., 2014; Kiani et al., 2021). The harmful effects of heavy metals in humans depend on their dosage, emission rate, and exposure period (Tchounwou et al., 2012; Balali-Mood et al., 2021). Heavy metals exposure can occur through various means, including consumption of contaminated food

and water, occupational ingestion or inhalation, and exposure to contaminated air and soil (Witkowska et al., 2021; Sarker et al., 2022).

The quality of irrigation water sources can significantly affect the concentrations of heavy metals in soil quality and cultivated vegetables (Rattan et al., 2005; Chaoua et al., 2019; Sharafi et al., 2022; Khan et al., 2023; Mohanty and Das, 2023; Soleimani et al., 2023). It can create a gradual accumulation of heavy metals in the soil, leading to soil and groundwater contamination. It can also lead to contamination of agricultural products and food. This can cause environmental effects on agricultural ecosystems and potential adverse effects on human health. Several studies have been carried out on the implications of using wastewater for irrigation resulting in the accumulation of heavy metals in soil and crops (Aydin et al., 2015; Chaoua et al., 2019; Mahfooz et al., 2020; Hilali et al., 2023).

In Meknes, Morocco, several studies have focused on microbiological contaminants in wastewater used for irrigation, highlighting their prevalence and the associated risks to health and the environment (El Addouli et al., 2012; Ouarrak et al., 2019; El Hassani et al., 2023). There are, however, significant gaps in research on metal pollution in relation to wastewater irrigation. In this context, this study is initiated to fill this gap by assessing heavy metal contamination in wastewater-irrigated farms and to identify potential risks for crop safety and human health in irrigated urban and peri-urban wastewater Meknes. The study focused on ten heavy metals Aluminum (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb), and Zinc (Zn). This approach consists of examining the heavy metal content in irrigation water, soil, and various vegetables produced on wastewater-irrigated farms to understand the extent and nature of the risks associated with using wastewater for irrigation in the Meknes region.

Materials and Methods

Description of the study area

The city of Meknes is located in the northwest of Morocco, 140 km east of the capital Rabat. Meknes is a part of the Fes-Meknes region, one of the 12 administrative regions of Morocco.

Smallholdings are located in the urban and periurban areas of Meknes city, mainly at three streams of water that cross the city: Ouislane, Toulal, and Boufekrane (*Figure 1*). Market gardening crops are the most produced in these areas. Arboriculture, small plots of forage, and livestock farming can also be found. Irrigation is mainly based on raw and mixed wastewater of various origins.

Sampling and analysis

Samples were collected from thirty farms in Meknes between November 2022 and May 2023, including irrigation water, soil at 15 cm and 30 cm depths, and six types of vegetables (*Table 1*). Sampling occurred 72 hours following the last irrigation event on each farm. Wastewater sources for irrigation varied; thirteen farms, primarily located in urban areas of Meknes, relied exclusively on domestic wastewater for irrigation purposes. In contrast, the remaining seventeen farms, typically found in the peri-urban expanses, utilized a combination of domestic and industrial wastewater.

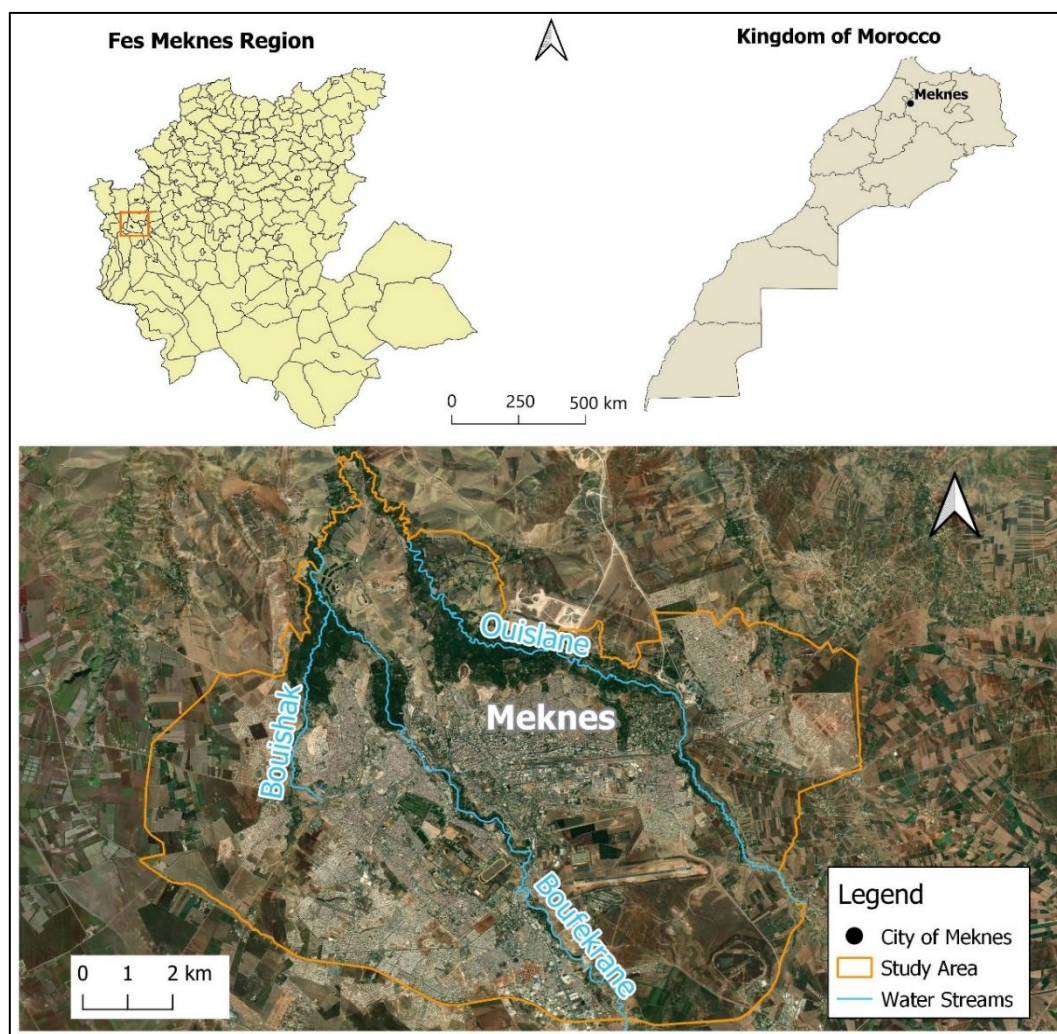


Figure 1. Geolocation of the study area

Table 1. Vegetables and Their Edible Parts Analyzed from Meknes Urban Farms

Name of crop	Scientific name	Edible part tested
Beet	<i>Beta vulgaris</i>	Root
Cardoon	<i>Cynara cardunculus</i>	Stems
Fava bean	<i>Vicia faba</i>	Seeds
Lettuce	<i>Lactuca sativa</i>	Leaves
Radish	<i>Raphanus sativus</i>	Root
Zucchini	<i>Cucurbita pepo</i>	Fruit

Water samples preparation

Water samples were meticulously collected from the study sites and subsequently filtered to eliminate any suspended solids. Aliquots of the filtered water samples were then treated with a nitric acid (HNO₃) procured from Sigma-Aldrich. Following this, the samples underwent mineralization, and the resulting solutions were then filtered, diluted with distilled water, and stored at a temperature of 4°C until they were ready for analysis.

Soil and vegetable samples preparation

To prepare the soil and vegetable samples for analysis, they were first rinsed with bidistilled water and dried at 70°C for 48 hours. Subsequently, they were finely ground into a powder for mineralization. Aliquots of 1g of dry weight were then subjected to treatment with a nitric acid (HNO₃). After mineralization, the samples were filtered, diluted with distilled water, and stored at 4°C until they were ready for analysis.

Heavy metals quantification

The quantification of the concentrations of the ten key heavy metals, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, was carried out according to the norms NF 11 885. using the ICP/AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) method. The instrument used for this analysis was the Ultima 2, manufactured by JobinYvon. This precise analytical technique ensured the accurate determination of heavy metal concentrations within the collected samples.

Quality control and assurance

Strict quality assurance and control measures were taken to ensure reliability of the study results. All reagents and chemicals used were of high purity.

Indices for risk assessment and crop safety

Heavy metal pollution index (HPI)

HPI is calculated to assess the overall quality of water with respect to heavy metals (Birch, 2013). An HPI value higher than 100 signifies that the contamination level exceeds the critical pollution limit and may pose a significant risk to health and the environment. The HPI is calculated using the following equation (Mohan et al., 1996):

$$HPI = \frac{\sum_{i=1}^n (Q_i \times W_i)}{\sum_{i=1}^n W_i} \quad (\text{Eq.1})$$

where n is number of heavy metals considered; (Q_i) is the measured concentration of ith metal in the water sample ; The Weightage factor to the heavy metal (W_i).

The Weightage factor (W_i) is calculated as:

$$W_i = \frac{K}{S_i} \quad (\text{Eq.2})$$

where S_i the standard permissible concentration for ith metal, K proportionality constant.

The enrichment factor (EF)

EF is a widely used metric for determining to assess the extent of metal contamination. EF values can be used to classify soils as deficiency to minimal enrichment ($EF < 2$), moderate enrichment ($2 \leq EF < 5$), significant enrichment ($5 \leq EF < 20$), very high enrichment ($20 \leq EF < 40$), or extremely high enrichment ($EF \geq 40$) (Mmolawa et al., 2011). Fe is a commonly used reference metal in many studies due to its consistent crustal abundance (Radomirović et al., 2020; Abd El-Aziz, 2021). The use of Fe as a normalizing element is common because it is uniformly distributed in the natural environment and has a consistent crustal abundance (Ravichandran et al., 1995). The upper crustal abundances

of trace elements are used (Hu and Gao, 2008). Calculation of enrichment factor was conducted according to the equation (Sinex and Helz, 1981):

$$EF = \frac{C_i}{C_{reference}} / \frac{B_n}{B_{reference}} \quad (\text{Eq.3})$$

where, C_i the measured concentration of the metal in the soil sample; $C_{reference}$ Concentration of Fe in the soil samples; B_n Background concentration of the metal of interest (upper crustal abundance); $B_{reference}$ Background concentration of Fe.

The index of geoaccumulation (I_{Geo})

Igeo is a widely used method to assess the degree of metal pollution in sediments and soil. The index provides an easy way to measure and classify the contamination levels of heavy metals (Abdullah et al., 2020). Igeo values can be used to classify soils as "Uncontaminated" ($I_{geo} < 0$), "Uncontaminated to moderately contaminated" ($0 \leq I_{geo} < 1$), "Moderately contaminated" ($1 \leq I_{geo} < 2$), "Moderately to heavily contaminated" ($2 \leq I_{geo} < 3$), "Heavily contaminated" ($3 \leq I_{geo} < 4$), "Strongly contaminated" ($4 \leq I_{geo} < 5$), or "Extremely contaminated" ($I_{geo} \geq 5$).

Using reference values, the (Igeo) calculates contamination relative to background levels. The Igeo is calculated using the following equation:

$$I_{geo} = \log_2 \left(\frac{C_i}{1.5 \times B_i} \right) \quad (\text{Eq.4})$$

where, C_i the measured concentration of the metal in the soil; B_i the background value of the metal; 1.5 the correction factor to account for potential variations in background concentrations due to lithological variations.

Contamination factor (CF)

CF is a measure of the overall degree of contamination of soil, by heavy metals. It is likely that it was developed as a way to provide a comprehensive measure of heavy metal contamination in soil. The classification for the contamination factor (CF) in sediments, where $CF < 1$ indicates a low degree of contamination, $1 \leq CF < 3$ is a moderate degree of contamination, $3 \leq CF < 6$ is a considerable degree of contamination, and $CF > 6$ is a high degree of contamination (Hakanson, 1980).

Calculation of the contamination factor CF was conducted according to the equation:

$$CF = \frac{C_i}{B_i} \quad (\text{Eq.5})$$

C_i the concentration of metal i in the soil; B_i the background concentration of metal i .

Pollution load index

PLI is an index used to evaluate the extent of pollution, particularly heavy metal pollution. A $PLI > 1$ indicates heavy metal pollution while a value < 1 suggests no pollution (Haynes and Zhou, 2022). The equation for PLI is as follow (Tomlinson et al., 1980):

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n} \quad (\text{Eq.6})$$

where CF_1, CF_2, \dots, CF_n is the contamination factor for each metal; n is the number of metals analyzed; n is the number of metals.

The metal pollution index (MPI)

MPI is an index used to evaluate the overall contamination level of heavy metals in vegetables. The MPI is calculated using the following equation (Usero et al., 1997):

$$MPI = (C1 \times C2 \times \dots \times Cn)^{\frac{1}{n}} \quad (\text{Eq.7})$$

where $C1, C2, \dots, Cn$ is the concentration of each metal; n is the number of metals analyzed.

Transfer factor (TF)

TF is a coefficient that quantifies the accumulation of heavy metals from soil to the edible parts of vegetables (Jolly et al., 2013; Prabasiwi et al., 2020). The equation to calculate TF can be represented as (Kachenko and Singh, 2006):

$$TF = \frac{C_{vegetables}}{C_{soil}} \quad (\text{Eq.8})$$

where $C_{vegetables}$ is the concentration of the metal in the vegetable; C_{soil} is the concentration of the metal in the soil.

Health risk assessment

The health risk assessment associated with the consumption of wastewater-irrigated vegetables involves the measurements of target hazard quotient, and hazard index.

Target hazard quotient (THQ)

The THQ is used to assess non-carcinogenic health risks for each individual heavy metal (USEPA, 2000). It's the ratio of the estimated daily intake (EDI) of a heavy metal to the reference dose (RfD) of that metal, which is the daily intake amount likely to be without appreciable risk over a lifetime (Table 2). THQ value is <1 , there is very little or no non-carcinogenic health risk. However, if the value is ≥ 1 , then there is a possibility that non-carcinogenic adverse health effects. The THQ is given by the following equation:

$$THQ = \frac{EDI}{RFD} \quad (\text{Eq.9})$$

where the EDI is calculated as:

$$EDI = \frac{MC \times IR \times EF \times ED}{BW \times AT} \quad (\text{Eq.10})$$

The Ef exposure frequency in days (365), Ed exposure duration in a life time (70 years), C mean concentration of the heavy metal (mg/kg). The BW is body weight (70 kg for an average adult), AT Averaging Time lifetime exposure for non-carcinogenic

effects (365 day \times 70 years). Daily vegetable intake rate is 0.0293 kg/day (Landais et al., 2015).

Table 2. Oral Reference Dose (RfD) Values of Heavy Metals

METAL	Oral Reference Dose mg/kg per day
Al	0.0005 (Joint F.A.O/W.H.O, 1989; Mahdavi et al., 2018)
As	0.0003 (Dayananda and Liyanage, 2021)
Cd	0.0005 (USEPA IRIS, 2011)
Cr	0.0003 (USEPA IRIS, 2011)
Cu	0.04 (USEPA IRIS, 2011)
Fe	0.007 (USEPA IRIS, 2011)
Mn	0.014 (USEPA IRIS, 2011)
Ni	0.02 (USEPA IRIS, 2011)
Pb	0.0035 (USEPA IRIS, 2011)
Zn	0.3 (USEPA IRIS, 2011)

Hazard index (HI)

The hazard index (HI) is a risk assessment metric that evaluates the potential risk posed by a combined exposure to multiple heavy metals (Sobus et al., 2018). The HI was calculated as follows:

$$HI = \sum THQ_{metals} \quad (\text{Eq.11})$$

When HI value is ≥ 1 , it foretells that there is possibility of non-carcinogenic adverse health effects while values that are < 1 depict very little or no non-carcinogenic effect.

Statistical analysis

The data were processed using Microsoft Excel Office 2019. For each metal, the average and the standard deviations were determined. These values were then compared to the Food and Agriculture Organization (FAO), the World Health Organization (WHO), and Moroccan guidelines for irrigation water quality. Similarly, soil comparisons were made with FAO, WHO, and United States Environmental Protection Agency (USEPA) norms. For vegetables, heavy metal concentrations were compared with the permissible limits set by the Codex Alimentarius of the WHO and the FAO.

Results

Assessment of heavy metals content in irrigation water

The Table 3 provides concentration limits of specific heavy metals in irrigation water from different organizations: WHO, FAO and Moroccan standards.

The evaluation of metal in irrigation water compared to Moroccan and other international guidelines content has revealed that the mean concentration of Al was found at 0.01 mg/l, considerably below the Moroccan limit of 5 mg/l, indicating a level of Al considered safe for irrigation. For As and Cd, the average concentrations were the same, at 0.01 mg/l each, both falling within the acceptable limits as per WHO, FAO and Moroccan. Cr presents a different result, with a measured concentration of 0.41 mg/l,

surpassing the thresholds set by FAO and European standards limit. Despite this, the levels are still under the Moroccan standards. Cu, Mn, and Zn show minimal levels at 0.01 mg/l, each, within the safety standards. Fe average concentration of 0.0779 mg/l is well below Morocco's limit of 5 mg/l. Contrastingly, levels are of significant concern, with an average concentration of 1.017 mg/l, which exceeds the international standards for safe irrigation water.

Table 3. Comparison of Heavy Metal Mean Concentration Limits in Irrigation Water from Wastewater-Irrigated Farms with International and National Standards

Heavy metals	Concentration (mg/l)	WHO Standard (mg/l)	FAO Standard (mg/l)	Moroccan standards (mg/l)	HPI
Al	0.01 ± 0.008	-	-	5	86.12
As	0.01 ± 0.012	0.01	0.1	0.1	
Cd	0.01 ± 0.007	0.01	0.01	0.01	
Cr	0.41 ± 0.34	-	0.1	1	
Cu	0.01 ± 0.008	2	0.2	2	
Fe	0.0779 ± 0.012	-	-	5	
Mn	0.01 ± 0.01	0.4	0.2	0.2	
Ni	0.01 ± 0.0018	0.02	-	2	
Pb	1.017 ± 1.41	0.01	0.1	5	
Zn	0.01 ± 0.006	3	2	2	

(-) not found

The HPI is a tool designed to assess water quality concerning heavy metal contamination in water bodies (Majhi and Biswal, 2016; Badeenezhad et al., 2023). The assessment of HPI value is 86.12, lower than the threshold of 100. This implies that irrigation water is primarily safe from heavy metal contamination.

Assessment of heavy metals content in irrigated soil

The following table presents the measured concentrations of various heavy metals in the soil samples under study. These values are compared with the established standards by the WHO, FAO, and USEPA.

The soil quality assessment revealed that Fe had the highest mean concentration at 3430.6 mg/kg, followed by Al at 1799.9 mg/kg and Mn at 62.269 mg/kg. Zn averaged at 13.749 mg/kg, Cr at 9.008 mg/kg, and Pb at 6.921 mg/kg. The average concentration of Cu was 4.567 mg/kg, whereas Ni was 3.08 mg/kg. Cd and As had the lowest mean concentration of 0.1 mg/kg. Currently, there are no universally established international limits for the levels of Al and Fe in soil. However, the concentrations of the remaining metals in the soil samples were within international safety standards (Table 4).

The persistence and bio-accumulative heavy metals nature, can pose significant ecological and health risks. Table 5 provides indices for a comprehensive assessment of the potential risks of heavy metal contamination in soil (EF, Igeo, CF and PLI).

EF is used to differentiate between anthropogenic sources of metal pollution and natural sources (Bern et al., 2019; Sappa et al., 2020). The examination of pollution indices for metal concentrations in wastewater-irrigated agricultural soil revealed that Cd and Pb emerged as prominent metals of concern, registering a high EF of 16.32 and 8.69, indicating a significant enrichment ($5 \leq EF < 20$). Additionally, Fe and Zn showed a

moderate enrichment with EF values of 3.74 and 3.206, respectively ($2 \leq EF < 5$). As for Igeo, all metals displayed negative values ($I_{geo} < 0$). However, Cd and Pb displayed the highest Igeo values, -0.58 and -1.60, respectively. The PLI value is less than 1, which indicates an absence of significant pollution in agricultural soil.

Table 4. Comparison of Heavy Metal Mean Concentration Limits in soil from Wastewater-Irrigated Farms with international Standards

Heavy metals	Concentration (mg/Kg)	WHO Standard (mg/Kg)	FAO Standard (mg/Kg)	USEPA Standard (mg/Kg)
Al	1799.9 ± 187.64	-	-	1000
As	0.1 ± 0.03	20	20	20
Cd	0.1 ± 0.05	3	0.3	0.3
Cr	9.008 ± 2.54	100	100	100
Cu	4.567 ± 1.02	100	100	1000
Fe	3430.6 ± 314.81	-	-	-
Mn	62.269 ± 19.40	-	1000	5000
Ni	3.08 ± 1.96	-	50	420
Pb	6.921 ± 1.55	50	50	400
Zn	13.749 ± 1.32	300	300	2000

(-) not found

Table 5. Metal Contamination Metrics in Soil

	EF	Igeo	CF	PLI
Al	0.36	-6.08	0.022	0.103
As	0.81	-4.91	0.05	
Cd	16.32	-0.58	1	
Cr	1.47	-4.06	0.09008	
Cu	1.35	-4.18	0.08304	
Fe	3.74	-4.61	0.0612	
Mn	1.06	-4.52	0.06554	
Ni	0.71	-5.09	0.044	
Pb	8.69	-1.60	0.49	
Zn	3.206	-2.93	0.196	

Assessment of heavy metals content in irrigated vegetables

The evaluation of heavy metal concentrations in different vegetable samples from our study area is illustrated in the figure below, showing the variations and accumulation patterns of these metals within the sampled vegetables.

For vegetable samples, beets had the highest Al concentration at 65.098 mg/kg, followed by lettuce with 13.757 mg/kg. Cardoon, fava beans, radish, and zucchini exhibited relatively lower Al concentrations, ranging from 1.975 mg/kg to 7.391 mg/kg. While there are no specific international standards for Al in vegetables, international guidelines exist for the tolerable intake of Al in food. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has set a Provisional Tolerable Weekly Intake (PTWI) of 2 mg/kg body weight for all Al compounds in food (Joint F.A.O/W.H.O., 2011). Notably, the concentrations of Al detected in vegetable samples from wastewater irrigated farms exceed these recommended tolerable intake levels.

As showed a uniform average concentration of 0.1 mg/kg across all vegetable samples, meeting the advisory limits recommended by health agencies from several countries, despite the absence of a global standard for arsenic in vegetables (McBride, 2013).

Cd average concentrations consistently register at 0.1 mg/kg, which aligns with the standards set by WHO. The maximum acceptable level for Cd is 0.2 mg/kg for leafy vegetables, 0.3 mg/kg for root vegetables, and 0.1 mg/kg for other vegetables (Codex Alimentarius Commission, 1995).

Cr average levels in all vegetables consistently remain at 0.1 mg/kg (Figure 2). There are no established maximum allowable levels for chromium in vegetables.

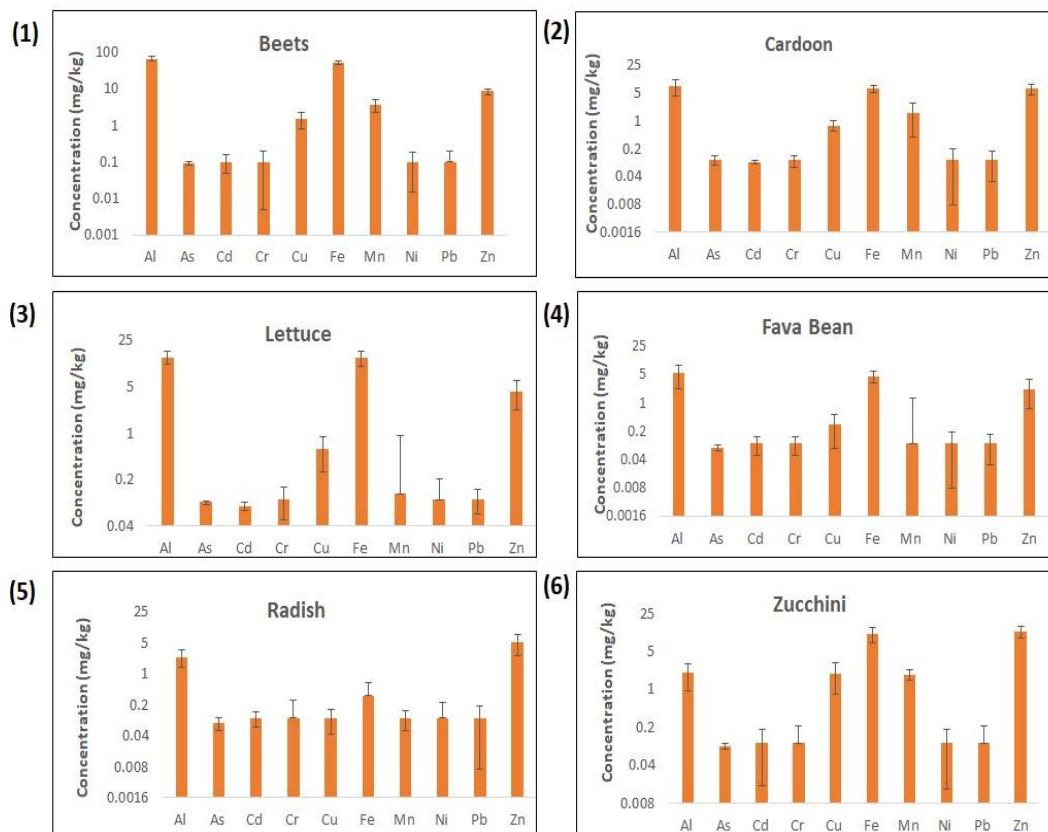


Figure 2. Heavy Metal Concentrations in Different Vegetables from wastewater irrigated farms (error bars represent standard deviation) ($p > 0.05$)

Cu concentrations in vegetable samples varied, with the highest level found in zucchini with an average of 1.963 mg/kg, followed by beets with 1.537 mg/kg and lettuce with 0.564 mg/kg (Figure 2). Cardoon and fava beans exhibit relatively lower Cu concentrations, ranging from 0.297 mg/kg to 0.751 mg/kg. Radish shows the lowest copper contamination at 0.1 mg/kg. None of the vegetable samples exceeded the recommended Cu limits for fruit and vegetables set at 40 mg/kg by the WHO/FAO (Joint F.A.O/W.H.O, 1999).

For Fe concentration, beets have the highest value of 50.828 mg/kg, followed by lettuce and zucchini, with concentrations of 13.55 and 10.499 mg/kg, respectively. Cardoon and fava bean show Fe levels of 6.514 and 4.575 mg/kg, respectively. Radish displays the lowest Fe concentration at 3.244 mg/kg (Figure 2).

Mn concentrations in the assessed vegetables were within safe limits as defined by WHO/FAO standards. Beets showed the highest Mn concentration at 3.567 mg/kg, while cardoon and Zucchini had lower levels, with 1.591 mg/kg and 1.853 mg/kg, respectively (*Figure 2*). Fava beans, lettuce, and radish were found to have the lowest Mn contamination, each with a concentration of 0.1 mg/kg. These values fall well below the WHO/FAO's permissible threshold of Mn less than 500 mg/kg (Joint F.A.O/W.H.O., 2011).

The average concentration of Ni found within vegetables was consistently reported at 0.1 mg/kg (*Figure 2*).

In all the vegetable samples (*Figure 2*), the average Pb concentration was 0.1 mg/kg, which aligns with the permissible limits (<0.3 mg/kg) set by WHO/FAO (Joint F.A.O/W.H.O., 2011).

Zucchini and beets exhibit the highest concentrations of Zn, recording values of 11.568 and 8.43 mg/kg, respectively (*Figure 2*). On the other hand, cardoon, radish, and lettuce register lower concentrations, with values ranging from 4.207 to 6.323 mg/kg. Fava Bean exhibits the lowest Zn levels among the vegetables, with a concentration of 2.26 mg/kg. All vegetable samples were within the acceptable limits (<60 mg/kg) (Åkesson et al., 2015).

The metal pollution index (MPI)

MPI is a quantitative measure that helps to assess the level of heavy metal pollution in plants (Mawari et al., 2022). We observed disparities in MPI values amongst different vegetables cultivated on wastewater-irrigated (*Figure 3*). It suggests inherent variations in their potential to accumulate metals under conditions of wastewater irrigation. Beets were the most affected among the investigated vegetables, exhibiting an MPI value surpassing 1.2. It was closely followed by Cardoon, who recorded an MPI value of about 1.06. In the mid-range, lettuce and zucchini presented values around 0.8. In contrast, both fava bean and radish displayed relatively lower propensities for metal accumulation, with respective MPI values of 0.627 and 0.606.

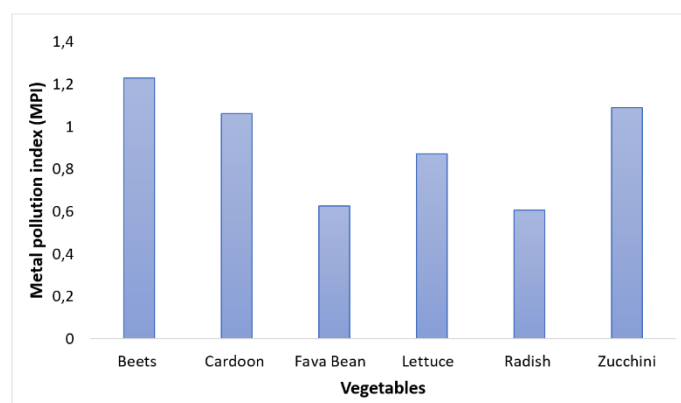


Figure 3. Metal pollution index (MPI) values of the total metal accumulation levels in Vegetables Cultivated on Wastewater-Irrigated Farms in Meknes

TF is an index used to assess the mobility of heavy metals from soil to plants (Prabasiwi et al., 2020). The TF value indicates the ability of plants to accumulate a particular metal from the soil into its tissues and to understand how much of a metal can

accumulate in the edible parts of the plant. Soil-to-plant transfer is one of the major pathways of human exposure to metal contamination (Jolly et al., 2013; Jalali and Meyari, 2022). The evaluation of TF is important for understanding the risk of heavy metal transfer to the edible plant when irrigated with wastewater.

As and Cd exhibit the highest TF, particularly in beets, cardoon, and zucchini, suggesting an elevated potential for bioaccumulation of these metals within these vegetables (*Figure 4*). Cu showed variability in transfer rate, with zucchini demonstrating a notably increased TF followed by beets. Similarly, Zn manifests variable absorption rates, with zucchini and beets again showing the highest TF, implicating these vegetables as more proficient in Cu and Zn uptake. These metals are essential for plant growth in trace amounts but can be toxic in higher concentrations. Conversely, TF for Al, Cr, Fe, Mn, Ni, and Pb are consistently low across the analyzed vegetables, indicating a limited translocation of these metals from soil to plant tissue.

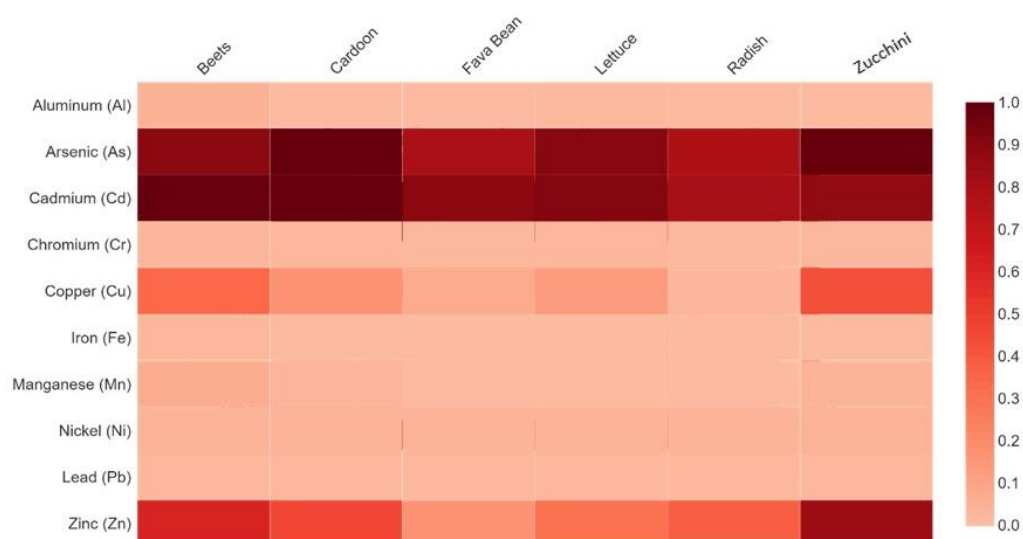


Figure 4. Transfer Factor Profiles of Heavy Metals in Vegetables Exposed to Wastewater

Health hazard assessment

The THQ serve as indicators of the potential health risks associated with the long-term consumption of metals found in various vegetables (Li et al., 2013).

Among the vegetables, beets demonstrate the most alarming profile (*Figure 5*). With a THQ of 14.84 for Al, this level is significantly above the threshold, implying that regular and prolonged consumption of beets could expose an individual to health risks due to Al. In addition, Fe in beets has a THQ of 3.039, which is also considerably above 1, suggesting potential health risks tied to Fe. Lettuce registers a THQ of 0.81 for Fe, nearing the threshold of concern. This indicates that consistent consumption of lettuce over time could also still be a health concern. Most of the metals in cardoon have THQ values well below 1, implying minimal risk. However, THQ of 1.68 for Al, could be potential concern if cardoon consumed frequently. Heavy Metals in Fava Beans generally pose minimal risk, with all THQ values below 1. However, THQ of for Al, exceeding the threshold, might be worth monitoring. Both radish and zucchini exhibit relatively low THQ values across all metals.



Figure 5. Target hazard quotient Profiles of Heavy Metals in Vegetables Exposed to Wastewater

One food may be contaminated with multiple heavy metals and the consumption of the irrigated vegetables may result in simultaneous exposure to the metals (Mawari et al., 2022). The HI provides a single value that represents the cumulative risk of exposure to multiple heavy metals (Badeenezhad et al., 2023). This method allows for the consideration of multiple heavy metals and their combined effect on human health, which is crucial given the common occurrence of multiple contaminants in the environment (Badeenezhad et al., 2023). *Figure 6* presents a Hazard Index analysis illustrating the comparative risk levels of heavy metal contamination across wastewater irrigated vegetables. A threshold line with an HI value of 1 delimits the point beyond which the level of risk is considered a significant health problem.

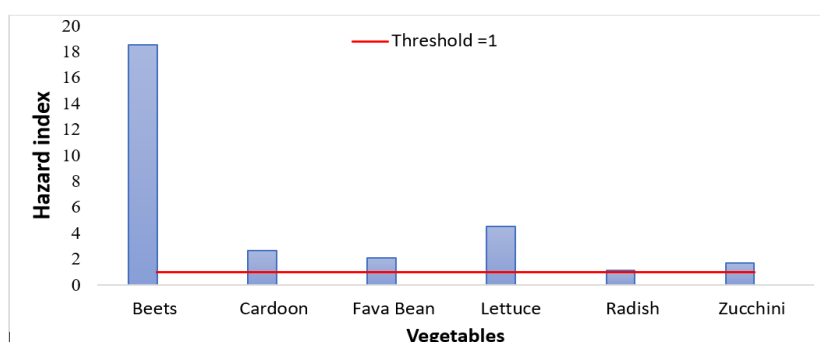


Figure 6. Comparative Hazard Index of Heavy Metal Contamination in Wastewater-Irrigated Vegetables

The HI for all the vegetables in the study exceeded the critical threshold of 1, indicating a potential health risk for consumers. Beets have the highest HI of 18.55, significantly above the other vegetables. Lettuce follows with an HI value of 4.49. Both fava beans and cardoon show HIs of 2.66 and 2.06, respectively. Zucchini and radish have lower but still concerning HI values of 1.7 and 1.11, respectively.

Discussion

The evaluation of metal content in irrigation water reveals that Al, As, Cd, Cu, Mn, and Zn are within the WHO, FAO and Moroccan standards. However, Pb and Cr average concentrations exceeded the international standards. This could be originated from industrial discharges effluent, urban runoff or the corrosion of pipelines (Ahmed et al., 2018). This is concerning due to their toxicity and the bio-accumulation. Exposure to these metals can have an effect on human health and the environment. Elevated levels of Cr can have an impact on plants growth and development. It has been reported that Cr contaminated soil had a lower agricultural production and quality (Zulfiqar et al., 2023).

Research consistently indicates that wastewater irrigation influences metal accumulation in agricultural soils. In Morocco, investigations have revealed a direct correlation between the practice of wastewater irrigation and increased levels of heavy metals in both soil and crops, as demonstrated in the work of Chaoua et al. (2019). Complementing these findings, Hilali et al. (2023) identified that in Beni-Mellal, the use of sewage water from the river is a significant factor in the heavy metal accumulation observed in agricultural soil.

Wastewater irrigated Soil heavy metal assessment showed hierarchy of metal concentrations $Fe > Al > Mn > Zn > Cr > Cu > Pb > Ni > Cd > As$. This is likely due to the natural abundance of Fe in biological systems. All heavy metals in soil were within the international safety standards, except for Al, which exceeded the USEPA standard. This can have beneficial and toxic effects on plant growth, depending on various factors such as soil pH, and the tolerance level of the plant (Bojórquez-Quintal et al., 2017).

Upon evaluating the pollution indices for metal concentrations from wastewater-irrigated agricultural areas, it was found that Cd and Pb are the most concerning metals showing a significant enrichment ($5 \leq EF < 20$), suggesting a dominant anthropogenic influence. The enrichment of these metals in agricultural soil indicates that the use of untreated wastewater effluent for irrigation, is contributing to heavy metal pollution in agricultural soil (Mahfooz et al., 2020; Akhtar et al., 2022). A study revealed that Pb accumulation in soil was higher in wastewater-irrigated soil than in groundwater-irrigated soil (Khalid et al., 2017). Cd and Pb are among the most toxic heavy metals that can cause serious health problems (Alengebawy et al., 2021; Balali-Mood et al., 2021; Collin et al., 2022). However, all metals assessed displayed a negative Igeo indicating that wastewater irrigated soil in Meknes is uncontaminated. The ranking of metals from the highest to the lowest Igeo value is as follows: $Cd > Pb > Zn > Cr > Cu > Fe > Mn > As > Ni > Al$. A negative Igeo values, combined with $PLI < 1$ as seen in this case, indicates that despite the presence of contamination, the overall soil quality is not polluted by heavy metals. However, metals like Cd and Pb, which have a high EF values, could be linked to specific sources of Cd and Pb, notably contaminated industrial wastewater effluent as well as urban runoff used for irrigation could be introducing these metals directly into the soil. The accumulation of heavy metals in wastewater-irrigated soil can pose a risk to human health. Their presence in agricultural soil can lead to accumulation in crops and entering the food chain. This was shown in a study conducted in Pakistan which reported that vegetables irrigated with wastewater had high metal content above the permissible limits (Khan et al., 2023).

Assessment of heavy metals in vegetables showed that Al is the only metal that exceed the limits recommended for vegetables. Al is considered to have low toxicity, but high exposure levels can lead to neurotoxicity and have been linked with neurodegenerative diseases like Alzheimer's (Skalny et al., 2021; Dey and Singh, 2022).

The comparative analysis of metal accumulation across different vegetables reveals that beets and cardoons are significantly more susceptible to metal pollution, with beets exhibiting the highest MPI. In contrast, radish shows a lower MPI. These observations align with the findings of (Kumar et al., 2020). These disparities in MPI values among the analyzed vegetables suggest inherent differences in their ability to accumulate metals when grown under conditions of wastewater irrigation. The higher MPI in beet could reflect the greater capability of beet to translocate metals from the soil to the edible parts. The difference in uptake could be attributed to variances in plant physiology, root structure, and the way every plant interacts with its environment (Ristova and Busch, 2014; Shen et al., 2017; Freschet et al., 2021). Beets tend to accumulate significant levels of heavy metals when grown in contaminated soils (Kumar et al., 2020; Boluspayeva et al., 2022).

The assessment of potential health risks using THQ and HI, showed that As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn had a THQ below the concern threshold, suggesting minimal non-carcinogenic risk from their consumption given the current conditions. This correlates with findings from Ethiopia, where despite long-term wastewater irrigation, heavy metals like Cd, Cr, Cu, Ni, and Zn remained within safe limits, with THQ values less than 1 (Woldetsadik et al., 2017). The alarmingly high THQ for Al in beets suggests a significant health risks associated with the consumption of this vegetable. The differences in Al THQ among various vegetables can be attributed to genetic variations which can have effect of metal uptake mechanisms and the differing ability of plants to translocate metals (Bojórquez-Quintal et al., 2017). Moreover, acidic soils increase the solubility and mobility of Al, thus elevating its uptake by plant roots (Panda et al., 2009). The THQ values of Al for other vegetables such as lettuce, cardoon and fava beans, though not as high as beets, still present a cause for concern $THQ > 1$. These levels suggest that even less affected vegetables may contribute to overall dietary exposure risks. THQ values suggest that the exposure level is potentially harmful over a lifetime of consumption. This could raise health concerns due to its known neurotoxicity and association with neurological diseases when present in high concentrations in the body (Fulgenzi et al., 2014; Skalny et al., 2021). Fe in beets also showed a high $THQ > 1$ while lower than Al, still indicates a potential risk.

The analysis of HI results suggests a potential health hazards with all the assessed vegetables had a HI values exceeding the threshold. The variation in HI values showed that beets had a significantly higher levels compared to other vegetables. These findings highlight that consumption of beets and lettuce, particularly over time, can pose non-cancerous health risks. With the complexity of wastewater irrigation practices, rigorous monitoring and regulation is needed to ensure the safety of irrigated crops.

Conclusion

The comprehensive assessment of metal content in irrigation water, soil, and vegetables in Meknes, Morocco, revealed a significant insight into the environmental and health implications of using wastewater for irrigation. This study revealed although the majority of metals are within acceptable limits, the specific elevation of Pb and Cr is of concern in irrigation water, exceeding international standards and involving notable health risks due to their toxicity and bio-accumulation.

The overall soil quality assessment was considered uncontaminated due to negative Igeo values and PLI of less than one. However, the specific enrichment of Cd and Pb suggests localized sources of contamination that need attention and action.

Evaluation of vegetables grown under these conditions reveals a concerning situation, especially for beets, which display the highest metal pollution index and a significantly high hazard index, indicating a profound susceptibility to metal pollution. The high THQ values for Al in beets imply that prolonged exposure to these vegetables may lead to adverse health effects for consumers. These implications highlight the need for stricter regulations, improved wastewater treatment systems, and careful monitoring of agricultural practices. It is important to implement regular control measures and monitoring to prevent contamination of agricultural products and ensure food safety. All stakeholders need to work together to mitigate public health risks and promote sustainable and safe agriculture in Meknes.

Conflicts of Interest. The authors declare no conflict of interest in relation to this article.

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