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Biosorption of Pollutants in Diyala River by Using Irrigated Vegetables

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Abstract: In the absence of environmental regulation, food stays to be contaminated with heavy metals, which is becoming a big worry for human health. The present research focusses on the environmental and health effects of irrigating a number of crops grown in the soils surrounding the Al-Rustamia old plant using treated wastewater generated by the plant. The physicochemical properties, alkalinity, and electrical conductivity of the samples were evaluated, and vegetable samples were tested for Cd, Pb, Ni, and Zn, levels, and even the transfer factor (TF) from soils to crops and crop and multi-targeted risk, daily intake (DIM) of metals, and health risk index (HRI) was calculated. The findings found that the average contents of Zn, Pb, Ni, and Cd in soil and vegetation were less than the Food and Agriculture Organization's standards of food safety enhancers. The flooded soil included Zn (56.5), Pb (15.1), Ni (9.30), and Cd (0.850) $mg{\cdot}kg^{-1}$. The heavy-metal concentration trend in all samples was Zn, Pb, Ni, and Cd. Daily metal intake in crops species was above acceptable limits for Zinc (0.011 – 0.019 $mg{\cdot}kg^{-1}$), Lead (2.010-5 – 5.910-5 $mg{\cdot}kg^{-1}$), Ni (2.410-4 – 5.210-4 $mg{\cdot}kg^{-1}$) and Cd (1.310-5 – 3.310-5 $mgkg^{-1}$). The HRI for zinc varied between 0.037 and 0.063, for lead between 5.10-3 and 1.410-2, for nickel from 1.210-2 to 2.610-2, and for cadmium from 1.310-2 to 3.310-2. The HRI for such components was larger than one, suggesting that no possible health issue existed. Crop cultivation using wastewater is a typical solution for water-stressed nations; nevertheless, previous screening and processing of such industrial wastewaters is required to minimise its detrimental effects on the environment.

Key words: Vegetables, toxic metals, health risk index.

Introduction

Environmental heavy metal contamination as well as food safety have grown to be major global problems in recent years. These substances, if obtained in large enough amounts to exceed ecological needs, can also have negative effects on the health of all living things, including humans in particular. There is a finite amount of natural water in Iraq. Since most of Iraq's arable land is situated in arid and semi-arid regions, it was imperative to look for alternate water sources that would help with the water budget and aim to establish an effective strategy for providing surface water and enhancing its effectiveness through the reuse of treated wastewater for irrigation purposes. Additionally, the introduction of numerous crop varieties was constrained, Due to the relatively easy accessibility, low cost, and limited source of water, wastewater becomes an alluring resource for

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agricultural irrigation, most often in urban areas, where the total area under cultivation in the local government areas where this grade of freshwater is used is 40.1 ha, representing for 7.1% irrigated lands (Kinuthia et al., 2020). Municipal or industrial wastewater is widely utilised for irrigation in developing nations (Gashi et al., 2020). Heavy metal buildup in field plants may be encouraged by long-term wastewater irrigation; heavy metals are classified as an environmental hazard due to their negative effects on animals, crops, and people, and is likely to harm cultures that are so close to such activities. Heavy metal concentrations that are too high often have negative effects on people, other animals, and the ecosystem as a whole. Acceptable permissible levels of heavy metals in food samples are connected to people's minor health issues (Golia and Diakoloukas, 2022). Fruits and vegetables cultivated on land supplied by heavy metal-polluted untreated wastewater provide a possible health concern to the public, and pollutants are likely the most common food contaminants (Nolos et al., 2022; Sall et al., 2020; Xu et al., 2022). Although they are not needed for plant development, heavy metals like Ni, Cd, and Pb are highly bioavailable and are retained by crops at lethal doses (Leblebici and Kar, 2018). The consumption of vegetable crops irrigated with waste water and cultivated on heavy metal-contaminated fields is harmful to both human and animal health (Mawari et al., 2022). Metal concentrations in the soil's solution play a key role in controlling the bioavailability of metals to plants. The majority of studies show that using irrigation water polluted with heavy metals for an extended period of time causes lands to have higher heavy metal concentrations than allowed (Dinu et al., 2021; Helmecke et al., 2020). Despite not being required for plant development, heavy metals like Ni, Cd, and Pb are extremely bioavailable and are retained by crops at lethal amounts. The consumption of vegetable crops irrigated with waste water and cultivated on heavy metal-contaminated fields is harmful to both human and animal health (Wellen et al., 2020). The majority of studies show that using heavily metal-contaminated waste water for irrigation for a lengthy period of time causes lands to have higher heavy metal concentrations than allowed.

Materials and Methods

The study was evaluated in 2019 in Iraq. This land is home to the Al-Rustumiya Sanitation WWTP, which has a capacity of 175000 m^3 day^{-1} and a population equivalent of 3 million. The cultivation lands were situated in latitudes N 33.274446, 33.262611, and longitudes E 44.53724, and 44.524999, respectively, at heights of around 454 and 379 m^2 above the sea high (Figure 1).

Water Treatment Sample Collection and Analysis

About 20 samples have been collected in plastic bottles (250 ml) sterilised with HNO_3 (Figure 1). The HNO_3 acid has been used to prevent microflora and maintain the samples collected. The samples were then processed using filter paper (Whatman 42) and stored in containers at 37°C until testing. To avoid erroneous results and contamination, the Ec and heavy metals, and pH were analysed using methodologies according to Sarkar (2015).

Figure 1: Map of example areas in Al-Ristmia surrounding the WWSP.

Sampling and identification of soil at random, eight comparisons were taken from each plant testing plot in the irrigated zone. In a clean plastic shopping bag, to create an individual composite sample, the samples were blended properly. A stainless steel hand soil auger was used to gather soil sub-samples at a depth of 0–20 cm. All objects in the laboratory were fully dry and passed through a 2-mm mesh filter under ambient settings. Stones, wooden, pieces, pebbles, gravels, and biological detritus were among the non-soil elements removed, pH and EC (Sarkar, 2015).

Plant Identification and Sampling

The principal crops and grains cultivated as millet (*Panicum miliaceum*), wheat (*Triticum turgidum*), and tomato (*Solanum lycopersicum*) served as botanical guides in the research area (*Solanum lycopersicum*). Three replications were used to harvest 500 g of each plant. Each vegetable was divided into leaf, root, and seed subsamples in the lab, and then thoroughly washed with distilled water to eliminate any visible dirt particles (Sarkar, 2015).

Heavy Metals Assessment

Before being crushed to powder, all samples were put at 72 hours in a 75°C oven. About 0.5 g of each soil and vegetable sample was digested for 24 hours at room temperature. After that, the mixture was cooked for 2 hours using the conventional manner (Sarkar, 2015). The digested samples were filtered through a 0.45 mm membrane after cooling, and the filtrate was diluted to 50 ml with deionized water and maintained at room temperature for analysis. The four heavy metal ions, Fe, Zn, Cd, and Pb, were detected in the filtrate of material using a Shimadzo atomic absorption spectrophotometer (AAS).

Deionized water was used to dilute a stock standard solution and prepare the heavy metal stock solution, 100 ppm of single element AAS higher quality results are used. The calibration curves for heavy metals were created with the use of AAS using known concentrations. WHO/FAO reference standard for heavy metal maximum limits (Ni (68 mg/kg), Zn (100 mg/kg), Cd (0.25 mg/kg) and Pb (0.35 mg/kg)) in irrigation soil, and vegetables was adopted for this study.

Data Analysis

Transfer Factor (TF)

Metal bioavailability in plants from soils might be predicted using a transfer factor, which is calculated as the proportion of metal ion level in crop to metal concentration in the soil (mg k^{-1}) (Miranzadeh et al., 2020).

$$TF = C_{edible}\ part/C_{soil} \quad (1)$$

where C_{edible} part and C_{soil} represent the levels of heavy metals in plant edible portions and soil, accordingly.

On a Daily Basis, Heavy Metals Consumed (DIM)

DIM, which is impacted by both metal concentrations in crops and the quantity eaten by the individual food product, was calculated using the equation:

$$DIM\ ¼\ C_{metal} \times C_{factor} \times D_{food\ intake} = B_{average\ weight}$$

where C_m, C_f, I_d, and B_w signify, respectively, the accumulation of heavy metals in plants, the reference value (fresh vegetable mass to dry vegetable weight), weekly vegetable intake, and mean body weight As stated in Miranzadeh et al. (2020), the factor 0.085 was used to change fresh green vegetable weight to dry weight. The daily vegetable consumption of children -adults was calculated to be 0.345 and 0.232 kg/person/day, respectively, with actual child body weights of 70.0 and 35.7 kg.

Health Risk Index (HRI)

DIM (daily metal intake) is calculated by dividing the reference oral dosage by DIM (daily metal intake), and the health risk index is calculated (RFD). This score assesses the danger posed to those who consume heavy metal-contaminated crops. Several vegetables can be consumed safely if the HRI score is less than 1 (Miranzadeh et al., 2020).

$$HRI = DIM/RFD \quad (2)$$

oral reference doses for Zn (0.3), Ni (0.02), Pb (0.004), and Cd (0.001) mg kg^{-1} day^{-1} (Miranzadeh et al., 2020).

The highest daily intake limit (mg $person^{-1}$ day^{-1}) for both adults and children is shown in Table 1.

Table 1: The maximum daily consumption limit (mg $person^{-1}$ day^{-1}) for both adults and children

Heavy metals	*Integrated risk information system*
Ni	1.00E+00
Cd	6.40E−02
Pb	2.40E−01
Zn	4.00E+01

Statistical Assessment

The Statistical Analysis Systems Computer Package was used to conduct statistical studies. In these studies, a fully randomised block design (CRBD) was utilised. The information was given as a mean and standard deviation. A paired t-test was used to compare levels of heavy metals first from the discharge point and the irrigation zone. At p 0.05, the least substantial change in heavy metal amounts in vegetables cultivated in irrigated areas was used to evaluate the intervention groups.

Results and Discussion

The pH of water samples obtained at the disposal site and the irrigation zone was 7.83 and 7.70, respectively. These readings are well within the irrigation-allowable. At the two sample locations, the median electrical conductivity of wastewater was 6.32 and 5.90 dS m^{-1}, respectively.

The median concentrations of heavy metals ($mg \cdot L^{-1}$) in wastewater varied among sites and were 0.137–0.100 for Ni, 0.168–0.150 for Zn, 0.009–0.009 for Cd and 0.227–0.220 for Pb. Pb had the highest concentration of heavy metals in the wastewater channel, followed by Ni, Zn, and Cd. The amount of Ni, Zn and Cd in the discharge did not exceed the allowed levels for heavy metals in irrigated agriculture. Pb, but on the other hand, surpassed the legal limit allowed by Iraqi law (Table 2). Heavy metals in drainage wastewater tend to accumulate in soils by becoming available to crops.

Table 3 shows the characteristics and concentration was determined of physicochemical factors in soils evaluated in irrigation areas. The soil samples had an average pH of 7.80. Heavy metal absorption and transport in soil are influenced by a variety of variables, including pH. Heavy metal accessibility diminishes when soil pH rises due to the precipitation of hydroxides and carbonates, and the development of non-soluble structures; soil pH has an influence on heavy metal mobility and bioaccumulation, and its adjustments are completely reliant on the pH of the irrigation wastewater.

The average electrical conductivity of the sample taken was 4.07 dSm^{-1}, indicating that was fairly salty, according to Singh et al. (2010). Increased conductivity has been shown to increase heavy metal solubility, resulting in accessibility of increased absorption of metals by the crop. The amounts of Cd, Zn, Ni and Pb in the soil were 0.850, 15.1, 9.30 and 56.5 $mg \cdot kg^{-1}$, respectively. The soil contained a high mean amount of Zn, preceded by Ni and Cd, and the concentration of dissolved Pb. The quantities of Cd, Ni, Pb, and Zn were observed to be decreased than reported and within the permissible limits specified by Mehmood et al. (2019). Heavy metal concentrations may be lower than permissible levels due to the constant removal of metals by food crops (vegetables and grains) cultivated in irrigated soil and also heavy metals penetrating deep soil (Shen et al., 2017)

Table 4 encapsulates the complex metal concentrations in the several plants that thrive in this area. According to data, all metals in food crops were found to be beyond permissible limits. Shen et al. (2017) revealed the greatest Fe and Zn levels and the lowest Pb concentrations in a variety of locally or imported created vegetable crops gathered from Baghdad, Iraq, comprising crops (turnips, carrots, potatoes, onions, lettuce and tomatoes). Millet had the lowest Zn concentration (30.3 $mg \cdot kg^{-1}$) while wheat had the highest (33.6) $mg \cdot kg^{-1}$. Millet seeds (0.048) mg/kg) and tomato (0.048) mg/kg exhibited the lowest and highest Pb (0.107) $mg \cdot kg^{-1}$ readings, respectively. Millet seeds had the lowest Ni concentration (0.579) $mg \cdot kg^{-1}$ while tomatoes had the highest (0.948) $mg \cdot kg^{-1}$. Tomatoes had the highest Cd levels (0.060) $mg \cdot kg^{-1}$ while wheat had the lowest (0.032) $mg \cdot kg^{-1}$.

The statistical results (Figure 2; Table 4) show the application of the insignificant difference (p0.05) in overall average heavy metal content across the plants.

Table 2: Physicochemical properties and heavy metal concentrations ($mg \cdot L^{-1}$) irrigation and wastewater from the disposal site

Parameters	*Irrigation area*	*Discharge point*	*P value*	*WHO/FAO standards for irrigation*	*Iraqi national limits*
Cd	0.009±0.007	0.008±0.004	0.141	0.018	0.024
E.C (dSm^{-1})	5.90±1.04	6.37±0.185	0.699	0.723 – 3.26	4.1
Ni	0.101±0.055	0.138±0.067	0.201	0.32	0.22
Pb	0.221±0.026	0.229±0.019	0.821	5.4	0.12
pH	7.70±1.15	7.87±0.797	0.911	6.7 – 8.1	4.5 – 8.9
Zn	0.150±0.047	0.171±0.029	0.645	2.11	2.31

Table 3: Heavy metal concentrations in soils from the wastewater-irrigated study area

Physico-chemical parameters mg·kg^{-1}	*E.C*	*4.09*	*
	Cd	0.88	2.8
	Ni	98	58
	Pb	157	303
	pH	73	*
	Zn	56.2	201

*Recommended concentrations in the soil

There are no significant variances between the other heavy metals, with the exception of zinc, which differs from the other elements investigated through the overall mean plants. Metal concentrations have demonstrated variances in plant capacity, which might be attributed to individual variability in uptake systems and heavy metal competition for absorption by various plants. Multiple heavy metals interacted at the root surface as well as within the plant, affecting heavy metal bioaccumulation. Numerous heavy metals interact at the root surface as well as within the plant. The intake and dynamics of diverse ions and chemically similar nonnutrient counterparts show that the affinity absorption of some ions is influenced by metabolic pathways engaged in root nutrient absorption. Summarising and formalised according to the current study and prior research (Golia and Diakoloukas, 2022; Shen et al., 2017), heavy metal poisoning affects plants cultivated on wastewater-irrigated soils, posing a health risk.

The results of the present investigation indicated the values of the bioconcentration factor from soil to crop samples. Zinc has the greatest BCF value of any element. Wheat soil has the greatest BCF of Zn, while in millet and tomato soil was 0.595 mg kg^{-1}, which have 0.536 , 0.469 mg·kg^{-1}. These BCF values were arranged as follows: Zn > Ni > Cd > Pb. Wheat has the highest BCF value of any crop sample, followed by millet and tomato, in that order. According to these data the BCF mean value differs significantly across the four metals; however, there is an insignificant difference for the three variations. Figure 3 shows that calculation of the bioconcentration factor (BCF) indicated that the accumulation of heavy metals in crop was in the order Zn > Pb > Ni > Cd. Pearson's correlation coefficient indicated the relationship between different elements content in soil and plant.

In order to establish the health risk index owing to heavy metal intake via crop eating, the level of input must be determined by examining the mechanisms of exposure levels to the particular species. Individuals can be exposed to pollution in a variety of ways, perhaps

Table 4: For heavy metal levels, multivariate analysis of mean comparisons by LSD, a 5% P value, and Sd.Err were used in edible produce parts (mg kg^{-1})

Plants	*Wheat*	*Tomato*	*Millet*	*Columns average*	*Guideline for safe limits*
Cd	0.032±0.010	0.060±0.003	0.042±0.007	0.045b	0.2
Ni	0.831±0.017	0.948±0.005	0.579±0.035	0.786b	5
Pb	0.062±0.013	0.107±0.004	0.048±0.016	0.072b	0.3
Zn	33.6±1.73	26.5±0.866	30.3±3.06	30.1a	50
Rows average	8.63a	6.90a	7.74a		

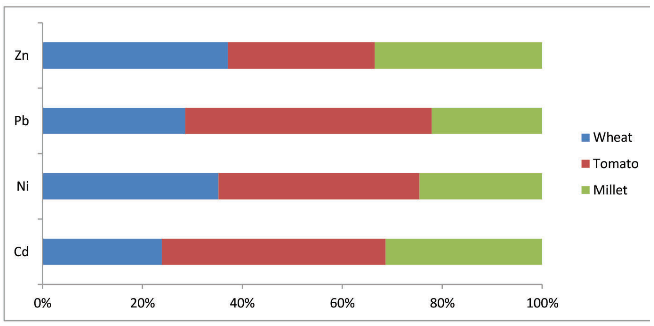

Figure 2: Histogram illustrating the change in heavy metals of Ni, Zn, Cd and Pb for a crop (Wheat, Tomato, Millet) grown in wastewater.

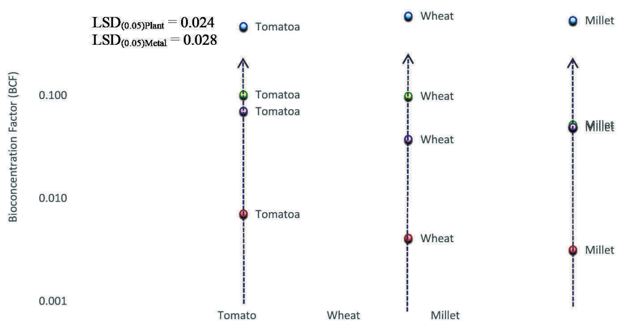

Figure 3: Crop cultivated in wastewater, the metals bioconcentration factor was calculated.

Table 5: Displays the daily metal intake (mg person^{-1} day^{-1}) HRI for a variety of heavy metals consumption of variety agricultural items developed in the research

Plants	*Individuals*	*Health risk index*	*Ni*	*Pb*	*Cd*	*Zn*
Tomato	Adults	DIM	0.0004	0	0	0.011
	Children		0.0005	0.0001	0	0.015
	Adults	HRI	0.02	0.011	0.025	0.037
	Children		0.026	0.014	0.033	0.05
Wheat	Adults	DIM	0.0004	0	0	0.014
	Children		0.0005	0	0	0.019
	Adults	HRI	0.017	0.0065	0.013	0.047
	Children		0.023	0.0085	0.018	0.063
Millet	Adults	DIM	0.0002	0	0	0.013
	Children		0.0003	0	0	0.017
	Adults	HRI	0.012	0.005	0.018	0.043
	Children		0.016	0.0085	0.023	0.057
*RDIM	mg person^{-1}day^{-1}		0.5	0	0	8
*UTDL	mg person^{-1}day^{-1}		1	0.24	0.064	40

* Heavy metals in foods: RDI and UTDL values.

one of the major heavy metal exposure pathways is through the supply chain. As a consequence, the DIM and HRI for children and adults were computed in order to study potential human health hazards in this region, and the findings are shown in Table 5. The DIM findings are in accordance with the Institute of Medicine's daily metal intake recommendations as well as the maximum acceptable UTDL. It was created by the Institute of Medicine for humans aged 19 to 70 years old (Golia and Diakoloukas, 2022). The regular metal intake in agricultural species for Zinc (0.011 – 0.019) mg·kg^{-1}, Lead (2.010-5–5.910-5) mg·kg^{-1}, Nickel (2.410-4 – 5.210-4) mg·kg^{-1} and Cadmium (1.310-5 – 3.310-5) mg·kg^{-1} is much lower than the required daily consumption and is within the maximum preliminary tolerated weekly consumption range (UTDL). Moreover, heavy metals demonstrate HRI1 for all crop species farmed in the research location, according to the report's findings (Table 5). HRI 1 implies that the exposed populace is free of metals-related health hazards, but HRI > 1 suggests that the intake of food crops may cause potential harm to human health. Singh et al. (2010) discovered that a collection of 7 different heavy metals (Pb, Cd, Cr, Zn, Fe, Cu, and Ni) irrigation water with varying water assets was determined in four distinct cash plants investigated, beans, pepper, onion, and tomato (tube well water, river water, and wastewater), and it was determined that (DIM) values were risk-free due to consumption of vegetables situated in various water supplies (Miranzadeh et al., 2020) analyses the hazard to the environment and human health associated with the use of Al-Rustamia factory treated effluent for vegetable irrigation; however, the average comprehensive pollution index (CPI) shows modest pollution across all seasons; however the average contaminants index (OPI) shows less pollution in the winter season, with contamination in other periods.

Conclusion

This investigation focussed on three distinct crops—wheat, millet, and tomato—that were watered with sewage from the Rustumiya facility in Baghdad State. Investigations were done into the deposition of Cd, Ni, Pb, and Zn in soils, wastewater, and different crops. It is plausible to assume that using wastewater for vegetable irrigation carries no immediate risk of heavy metal contamination because the routine discharge of untreated agricultural regions over a number of years has led to the buildup of heavy metals in soils and plants. Although crop pollution varied from the FAO/WHO permissible level, the study's findings clearly demonstrate that irrigated wastewater-soils increased the contamination with Cd, Ni, Pb, and Zn. Therefore, eating these veggies results in long-term low-level heavy metal deposition in the body, which has negative effects; this has been evident after several lengthy exposures.

According to the Health Risk Index, the majority of crops were not polluted with Cd, Ni, Pb, or Zn, and there was no danger to human health from ingesting plants cultivated at this location for an extended length of time using irrigation made from wastewater. Thus, this region is in need.

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