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Bioaccumulation of heavy metals in the different parts of maize cultivated

in soils irrigated with different quality of water



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Abstract

The present study investigated the bioaccumulation and distribution pattern of heavy metals in maize organs cultivated in soils with varied levels of heavy metals. Additionally, the potential human risk due to the ingested levels of heavy metals detected in maize grains was studied. Nine locations, representing soils irrigated by different water sources of fresh and wastewater, were selected. Heavy metals analysis was carried out using inductively coupled plasma method with optical emission spectrometry (ICP-OES). The results revealed that heavy metals of Ni, Cu and Cr were the most abundant elements detected in the studied soil sites followed by Pb and Cd. Values of the total uptake of heavy metals by maize from the soils irrigated by wastewater were 3.3-5.6 folds those of soils irrigated by fresh water. Soils irrigated with wastewater showed bioaccumulation factor (BF) averages for heavy metals in maize at the following descending order: Pb > Cd > Ni > Cu > Cr. Meanwhile, soils irrigated by the river or groundwater exhibited BF values arranged as Cu = Ni > Cr > Cd > Pb. The accumulation pattern of heavy metals in maize organs was arranged as: roots > leaves > stem > cob > grains. As well, except for Ni, levels of all heavy metals, in maize grains, were lower than the permissible limits set by FAO/WHO. Notably, the rank order of hazard quotient to heavy metals was Cd > Pb > Ni > Cu > Cr; with low potential risk for public health.

Keywords: Maize; contaminated soil; heavy metals; bioaccumulation; translocation; risk assessment

1. Introduction

Soil contamination by organic and inorganic pollutants has been widely spread worldwide due to the industrial activities and agricultural practices such as application of farm-animal manure, application of fertilizers and pesticides, wastewater irrigation, and soil-sludge amendment [1, 2]. The accumulation of heavy metals in soil over time may affect the physicochemical characteristics of soil as well as yield and quality of the agricultural products and ecosystem [3-5]. Subsequently, the translocation of heavy metals to plants may have major problems that can threaten the safety of food and public health [5, 6]. Because heavy metals are persistent in both the freshly-eaten vegetables and fruits and in the processed food products of plant-based [7, 8]. In particular, heavy metals can enter plant tissues such as roots, stems, leaves and grains, and these metals are transferred into animal and human systems resulting in serious health problems such as cellular damages, carcinogenesis and Alzheimer's diseases [9].

The bioaccumulation of heavy metals in plants is influenced by several factors including; fertilization, levels of heavy metals in the soil, the nature of soil and plant selectivity [10]. For example, many phosphate rocks contain Pb and Cd, and the application of phosphorus fertilizer, with high rates, leads to the increase of its content in plant above the maximum permissible limit [11, 12]. Also, Wangstrand et al. [13] revealed that application of the nitrogen fertilizers was associated with an increase in

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Cd concentration in wheat.

Maize (*Zea mays* L.) is an edible flowering plant belonging to Poaceae family and grown during the spring and summer seasons in Egypt. Maize is considered one of the economic cereal crops all over the world, whether in human nutrition or animal feeding [14]. In Egypt, maize represents about 25% of the cultivated area (888,329 hectares) and occupies the third place in production of crops after wheat and rice with an average yield of 7.80 ton ha-1 [15]. Maize grains can be grilled and directly eaten, and it can be ground and blended with wheat flour to be used in the preparation of bread.

Opaluwa et al. [16] studied the translocation of some heavy metals from soil to maize grains grown on different regions in Nigeria. They reported that the concentration of heavy metals in soil samples ranged from 0.32 to 0.84 (mg kg⁻¹) for Cd, 0.34 - 0.91 (mg kg⁻¹) for Cu, 0.21 - 0.42 (mg kg⁻¹) for Ni and 0.1 -0.53 (mg kg⁻¹) for Pb. Meanwhile, the levels of these metals in maize grains were in the range of 0.04 -0.14, 0.03 - 0.48, ND - 0.01 and 0.02 - 0.23 (mg kg⁻¹) for Cd, Cu, Ni and Pb, respectively. In addition, Lu et al. [17] determined Cr, Pb and Ni in different parts of maize plant. They found that the distributed concentrations of Cr were 105.2, 9.3, 15.6 and 0.23 (mg kg⁻¹) in root, stem, leaves and grains, respectively. Meanwhile the levels of Pb and Ni in root, stem, leaves and grains were less than Cr as 5.12, 1.25, 3.57 and 0.49 mg kg⁻¹, respectively for Pb, as well as 6.56, 1.61, 1.40 and 0.18 (mg kg⁻¹) for Ni respectively.

Recently, with the development of established agriculture, agricultural areas rapidly increased all over the world. However, up to now, heavy metals content of the agricultural soil in Egypt is progressively studied; nevertheless, there is no systematical investigation for translocation of heavy metals from agricultural soils to plant parts. Therefore, the current investigation was designed to study the effect of soil characteristics and it's heavy metals content on the total uptake and bioaccumulation factor of heavy metals in maize cultivated in Egyptian soils receiving two kinds of irrigation water; fresh water (Nile River water and groundwater) and contaminated water by industrial effluents and sewage wastewater. Additionally, to study the distribution pattern of heavy metals among the different organs of maize (roots, stem, leaves,

cob, and grains) when cultivated in soils with different characteristics. Finally, to study the safety of maize grains by evaluating its contents of heavy metals based on the recommended permissible limits.

2. Materials and methods

2.1. Sampling

A total of 27 maize plant samples and 27 soil samples (sampling depth 0-30 cm) were collected from nine different locations representing three Egyptian Governorates (Giza, Kafr-Elsheikh and El-Beheira, three different locations for each) during August, 2018. Samples of Giza Governorate were collected from Abdel-Rahman zone that is irrigated by groundwater, while Kafr-Hakem and Abou-Roash zones are irrigated by sewage-contaminated water. The samples of Kafr-Elsheikh Governorate were collected from Al-Hawia zone which is irrigated by the Nile River water, while Kafr Dokhmais and Al-Nasiria zones are irrigated with industrial effluentscontaminated water from Kitchener drain. Samples of El-Beheira Governorate were collected from Wadi El-Natron, El-Nobaria (Abdel-Rakib) and El-Nobaria (Abdel-Wahab) zones that are irrigated with the Nile River water.

2.2. Soil physicochemical analysis

Soil particle size distribution was determined by the pipette and dry sieving methods for the heavy and light-textured soils, respectively, according to Klute [18].

Soil chemical characteristics were determined according to Page et al. [19] as follows: Soil reaction (pH) was measured in soil paste using a glass electrode. The electrical conductivity (EC), in dSm⁻¹ at 25 °C, was determined in soil paste extract, while organic matter (OM) content was determined by oxidation with potassium dichromate according to the method of Walkely and Black [20].

2.3. Digestion of maize samples

Digestion of the different parts of maize plant was applied according to Briscoe [21] as follow: 5 grams of the crashed samples for each maize part were weighed into a sealed crucible then dried in an oven set at 105°C. Dry-ashing process was carried out in a muffle furnace by stepwise increase of the temperature up to 550 °C for 5 h until the sample was completely combusted (gray or slightly colored). The ash was dissolved using 1 mL concentrated HCl at crucible walls, and then transferred to a volumetric flask (25 mL) by de-ionized water to complete volume. The ash suspension was filtered through an ash-less filter paper Whatman No. 42 and stored in a refrigerator until determined by Inductive Coupled Plasma–Optical Emission Spectrometry (ICP-OES).

2.4. Digestion of soil samples

Digestion of the soil samples was applied according to Allen et al. [22] as follow: 0.5 g of airdried ground soil was weighed into a kjeldahl flask then digested with 1 mL HClO₄ (60%), 5 mL concentrated HNO₃ and 0.5 mL concentrated H₂SO₄ for 10-15 min until the appearance of white fumes. After cooling, the content was filtered through a Whatman No. 4 ash-less filter paper and diluted to a volume of 50 mL with distilled water. The filtered solution was analyzed using the ICP apparatus.

2.5. Heavy metals analysis

The operating conditions for heavy metals analysis were adopted according to APHA [23] using the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES (inductively coupled plasma with optical emission spectrometry), with Agilent Vapor Generation Accessory VGA 77. For each series of measurements intensity calibration curve was composed of a blank and three or more standards from Merck Company (Germany). Accuracy and precision of the Cd, Pb, Ni, Cr and Cu ions' measurements were confirmed using external reference standards from Merck, and standard reference material and quality control sample, from National Institute of Standards and Technology (NIST), were used to confirm the instrument reading.

2.6. Uptake and bioaccumulation

The total uptake of each element by maize was theoretically obtained by calculating the sum of the element contents in all maize parts (root + stem + leaf + cob + grain). While, the bioaccumulation factor (BF) was calculated by dividing the total content of the element in maize parts by its content in the soil according to the following equation:

$$BF = C_{plant} / C_{soil}$$
 [24].

C_{plant}: total content of the element in maize (dry weight basis).

C_{soil}: the element content in soil (dry weight basis).

2.7. Risk assessment of exposure to heavy metals

The estimated daily intake (EDI, μ g) of every metal from maize (grains + flour) consumption was calculated as follows:

$$EDI = \frac{Cf \times Occ}{BW}$$

Where: Cf is the daily corn consumption (g/person), Occ is the occurrence of heavy metal in maize grains expressed as (µg contamination/g maize) and BW is the mean body weight for an adult person (70 kg). The daily consumption from maize grains + maize flour (106.2 g/day) was obtained from WHO [25]. Three levels of EDI were calculated for the lowest, average and highest detected concentrations.

Values of tolerable daily intake (TDI) for (Pb and Cd) and (Cu, Ni and Cr), as µg/kg bw/day, were obtained from FAO/WHO [26] and Baars et al. [27], respectively.

Hazard Quotient (HQ) was calculated as follows:

$$HQ = \frac{EDI}{TDI}$$

When HQ value is lower than 1, it refers to a safe range. While for HQ value higher than 1, adverse health effects are considerable [28].

2.8. Statistical analyses

Results were subjected to one-way analysis of variance (ANOVA) of the generalized linear model (GLM) using SAS statistical package [29]. The results were the average of three replicates ($p \le 0.05$).

3. Results and Discussion

3.1. Soil physicochemical characteristics

Obtained results in Table (1) showed that the pH values of the studied soils were alkaline (pH range:

8.29-8.95) with slight differences between the selected locations. These slight differences in pH values may be ascribed to the different sources of irrigation water as reported by Abuzaid [30], where the soil pH depends on the basic ions content (Ca^{2+} , Mg^{2+} , K^+ and Na^+) in irrigation water [31]. These results were in agreement with those of Abou-Shanab et al. [32], who stated that the pH of Egyptian soils is generally located in the alkaline range (7.7-8.3). Mahmoud and Ghoneim [33] found that the pH value of soils irrigated by contaminated water (in El-Mahla El-Kobra) were in the range of 7.80-8.50. Seleiman and Kheir [34] found that soils of Kafr Elsheikh Governorate, North Nile, Delta, Egypt were alkaline (pH range: 7.90-8.58).

Regarding the electrical conductivity (EC) values, it was conspicuous that except for the slightly saline soil collected from Kafr-Dokhmais zone, all the other soils were non-saline ($< 1 \text{ dSm}^{-1}$: 0.21–0.98 dSm⁻¹) according to EC thresholds described by Dahnke and Whitney [35] as well as Smith and Doran [36]. Generally, soils irrigated with the contaminated water by industrial effluent and sewage showed the highest EC levels as confirmed by Khaskhoussy et al. [37] and Mollahoseini [38] who stated that irrigation by sewage water increased the soil salinity, where the soluble salts of the low-quality water are particularly accumulated in the surface soil layers [39].

As for the OM content, the richest soil site was Al-Hawia (4.11%) followed by Kafr-Dokhmais and Al-Nasiria sites. However, soil samples of Abdel-Rahman and El-Nobaria (Abdel-Wahab) zones markedly had the lowest OM contents (0.34 and 0.51 %), respectively. These results possessed similar trend to previous studies of Abou-Shanab et al. [32] as well as Seleiman and Kheir [34] who reported that the OM contents of the Egyptian soils of Delta varied from 0.62 to 4.1 (%).

Meanwhile, the clay content was highest in Al-Hawia soil (47.2%) followed by soil samples of Kafr-Dokhmais and Al-Nasiria sites which were 45.2 and 41.2 (%), respectively. The other soil samples had a clay percentage in the range of 7.2-19.2(%). Similar results were obtained by Abou-Shanab et al. [32]. Of course, silt and sand are complementary ingredients to OM and clay that forming the soil texture, where soils with the highest contents of OM and clay have the lowest contents of silt and sand as compared to other soils. Generally, soil texture of the studied

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samples varied between sandy (reclaimed soil), loamy sand, and clay soils.

3.2. Uptake and bioaccumulation of lead and cadmium in maize

Data presented in Table (2) exhibited that soils irrigated with either the Nile River water or groundwater had comparable contents of Pb ranged between 1.77 and 3.79 (mg kg⁻¹), which were significantly lower than those irrigated from an industrial effluents-contaminated water, Kitchener drain, $(6.49 - 7.33 \text{ mg kg}^{-1})$ or from sewage wastewater (4.56 and 5.88 mg kg⁻¹).

Cadmium contents in soils had the same trend of Pb, Wherein the irrigated soils by the Nile water and groundwater (Wadi El-Natron, Abdel-Rakib, Abdel-Wahab, Al-Hawia and Abdel-Rahman) showed the lowest Cd levels (0.40 and 0.55 mg kg⁻¹). In case of soils irrigated with wastewater of industrial effluents and sewage (Kafr-Dokhmais, Al-Nasiria, Kafr-Hakem, and Abu-Roash), the Cd levels were two or three times greater than those irrigated with fresh Nile water and ground water (0.85 to 1.67 mg kg⁻¹).

The obtained results of heavy metals in soils, irrigated by the Nile and ground waters, were comparable to those of Mirecki et al. [40] who found that concentrations of Pb, Cd and Cu in non-polluted soil were 4.61, 0.05 and 7.16 (mg kg⁻¹), respectively. Also, the results were in agreement with those obtained by Chen et al. [41]; El-Gendi et al. [42] and Abou-Shanab et al. [32] who stated that the soil irrigated by polluted industrial wastewater had higher levels of heavy metals than those irrigated by fresh water. However, our results were markedly lower than those reported by Mahmoud and Ghoneim [33] for the levels of heavy metals in the soils surrounding Zefta drain and drain no. 5 (adjacent sites to our study zone of Kafr-Dokhmais). Their reported levels of Pb and Cd were 48-92 and 13-33, respectively. The wide difference between our results and their results may be due to the high levels of heavy metals in Zefta drain and drain no. 5 as compared to those in the Kitchener drain close to Kafr-Dokhmais zone.

Table 1. Physicochemical characteristics of the studied soils

Source of irrigation water	Zone	pH (1:2.5)	EC dSm ⁻¹ (1:5)	OM (%)	Clay (%)	Silt (%)	Sand (%)	Soil texture
	Wadi El-Natron	8.86	0.265	2.21	15.2	12	72.8	Loamy sand
Nile Biyen weten	El-Nobaria (Abdel-Rakib)	8.55	0.283	2.41	13.2	6	80.8	Loamy sand
Nile River water	El-Nobaria (Abdel-Wahab)	8.95	0.225	0.51	7.2	4	88.8	Sandy
	Al-Hawia	8.45	0.214	4.11	47.2	32	20.8	Clay
Groundwater	Abdel-Rahman	8.63	0.229	0.34	9.2	2	88.8	Sandy
Contaminated water by industrial effluents	Kafr-Dokhmais	8.29	2.290	3.96	45.2	32	22.8	Clay loamy
	Al-Nasiria	8.48	0.979	3.60	41.2	36	22.8	Clay loamy
Contaminated water by sewage	Kafr Hakem	8.42	0.905	1.77	11.2	6	82.8	Loamy sand
	Abu-Roash	8.37	0.961	1.53	19.2	9	71.8	Sandy loamy

EC: electrical conductivity OM: organic matter

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Table 2. Concentrations of lead and cadmium in the soil and its bioaccumulation in maize

		Lead			Cadmium			
water	Zone	Soil (mg kg ⁻¹)	Plant's total uptake (mg kg ⁻¹)	BF*	Soil (mg kg ⁻¹)	Plant's total uptake (mg kg ⁻¹)	BF	
	Wadi El-Natron	$2.65 \ ^{\rm f} \pm 0.07$	1.06	0.40	$0.527 e \pm 0.023$	0.374	0.71	
	El-Nobaria (Abdel-Rakib)	$1.77 ^{g} \pm 0.06$	0.90	0.51	$0.433~{\rm f} \pm 0.023$	0.210	0.48	
Nile river water	El-Nobaria (Abdel-Wahab)	$1.93 \ ^{g} \pm 0.06$	0.96	0.50	$0.400~{\rm f}\pm 0.025$	0.318	0.80	
	Al-Hawia	3.79 ° ± 0.12	1.95	0.51	$0.550^{\ e} \pm 0.023$	0.448	0.81	
Groundwater	Abdel-Rahman	$2.53 \ {}^{\mathrm{f}} \pm 0.08$	1.39	0.55	$0.553^{e} \pm 0.020$	0.274	0.50	
Contaminated water by industrial effluents	Kafr-Dokhmais	7.33 ^a ± 0.15	6.79	0.93	1.260 ° ± 0.026	1.154	0.92	
	Al-Nasiria	$6.49^{b} \pm 0.11$	5.70	0.88	$1.667 \ ^{a} \pm 0.027$	1.464	0.88	
Contaminated water by sewage	Kafr Hakem	$4.56^{\ d} \pm 0.06$	3.69	0.81	$0.853 \ ^{d} \pm 0.020$	0.709	0.83	
	Abu-Roash	$5.88 \ ^{c} \pm 0.17$	5.41	0.92	$1.453 \ ^{b} \pm 0.032$	1.235	0.85	
LSD		0.32			0.074			

*BF: Bioaccumulation factor. Means followed by different subscripts within column are significantly different at the 5% level.

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For the total uptake of Pb and Cd by maize, a positive correlation was observed between the soil element content and the adsorbed amount of the element by the plant. The concentration of an element in the plant depends on the relative level of exposure from a contaminated soil in addition to the phytoavailability and deposition of the element from the polluted air [40, 43, 44]. Briefly, the total Pb and Cd values in maize irrigated by the Nile and ground waters were in the range of $(0.90 - 1.95 \text{ mg kg}^{-1})$ and $(0.21 - 0.45 \text{ mg kg}^{-1})$, respectively. Meanwhile, maize plants irrigated with industrial effluents and sewage wastewater exhibited elevated levels of both Pb and Cd, which ranged between (3.69 - 6.79 mg kg⁻¹) and $(0.71 - 1.46 \text{ mg kg}^{-1})$, respectively. Aremu et al. [45] reported that the total amount of Pb takenup by maize, cultivated in a mining area in Nigeria, was 0.32 mg kg⁻¹, while Cd was not detected.

Concerning the BF values, it was clear that the BF values of Pb in maize cultivated in soils irrigated with industrial effluents and sewage wastewater represented the highest values as compared to the other irrigation sources. These high levels were comparable (average: 0.81 - 0.93). However, the BF values of Pb in maize irrigated with the Nile and ground waters were low (half values of the industrial and sewage water) and comparable (average: 0.40 -0.55). Bioaccumulation factor for Cd in maize irrigated with the industrial and sewage waters were similar to those of Pb in the same maize samples which verified the same accumulation pattern for both elements. Also, the BF values of Cd in maize irrigated with wastewater were two times greater than the values of maize irrigated with the Nile and ground waters except for 3 sampling sites (Wadi El-Natron, Abdel-Wahab, and Al-Hawia). In general, although the soils contents of Pb and Cd were different, however the BF values of both elements were so far similar except for 3 soil sites which possessed BF values for Cd being double those of Pb. The 3 soil sites irrigated from the Nile water were Wadi El-Natron, Abdel-Wahab and Al-Hawia.

3.3. Uptake and bioaccumulation of copper, nickel and chromium in maize

Regarding the bioaccumulation of Cu, Ni and Cr, their concentrations in soils and maize were shown in Table (3). The soil of Kafr-Dokhmais, which were irrigated by an industrial effluents-contaminated water, had the highest Cu content being 40.04 mg kg-¹. In addition, there was no significant difference in Cu contents between the soils of Al-Nasiria (industrial effluents-contaminated water) and Kafr-Hakem (sewage-contaminated water) which were 33.77 and 34.37 (mg kg⁻¹), respectively. On the other hand, soil sites irrigated with the Nile and ground waters contained low Cu levels varied between 5.10 and 13.16 (mg kg⁻¹). Three sites out of 5 had comparable levels (5.10-6.84 mg kg⁻¹); however, the remaining 2 sites (Wadi El-Natron and Al-Hawia) possessed significant values being 12.51 and 13.69 (mg kg⁻¹), respectively. Data of Ni and Cr contents had the same trend of Cu, where soil sites irrigated with contaminated water, by industrial effluents or sewage, contained the highest detected concentrations of Ni and Cr. These Ni and Cr concentrations were significantly higher than those detected in soils irrigated from the Nile and ground waters. The obtained results were in accordance with those of El-Gendi et al. [42] who found that the sandy soil of Abou-Roash area had elevated levels of Fe, Cu and Zn, which reached 5, 125, and 170 times that of the virgin soil in the same area as a result of irrigation by drainage water. Furthermore, Mahmoud and Ghoneim [33] reported high levels of Cu and Ni, in the soils surrounding Zefta drain and drain no. 5, were 82-386 and 55-164 (mg kg⁻¹), respectively.

The total uptake of Cu, Ni and Cr by maize received the Nile and ground waters irrigation were in the ranges of $(3.67 \text{ and } 9.89 \text{ mg kg}^{-1})$, $(3.35 \text{ and } 9.89 \text{ mg kg}^{-1})$ 9.96 mg kg⁻¹) and (2.25 and 7.70 mg kg⁻¹), respectively. Meanwhile, maize, irrigated by the industrial and sewage wastewater, had taken up the highest amounts of Cu, Ni and Cr as disclosed in Table (3). These results did not match with those of Aremu et al. [45] who reported that the total taken-up amounts of Cu, Ni and Cr by maize, cultivated in a mining area and irrigated with a contaminated water, were 2.05, 1.04 and 1.36 (mg kg⁻¹). These amounts were markedly lower than obtained results for both maize samples irrigated either with fresh water or contaminated water. Although, the soil surrounding the mining area tends to contain high levels of heavy metals, however they may be occurred in a low bioavailability-form in the studied soil.

		Copper			Nickel			Chromium		
Source of irrigation water	Site	Soil (mg kg ⁻¹)	Plant's total uptake (mg kg ⁻¹)	BF*	Soil (mg kg ⁻¹)	Plant's total uptake (mg kg ⁻¹)	BF	Soil (mg kg ⁻¹)	Plant's total uptake (mg kg ⁻¹)	BF
	Wadi El-Natron	$12.51 \ ^{d} \pm 0.16$	9.27	0.74	$5.34^{\rm \; f} \pm 0.22$	3.35	0.63	$11.93 ^{\text{d}} \pm 0.21$	7.70	0.65
Nile River water	El-Nobaria (Abdel-Rakib)	$5.72 \ ^{f} \pm 0.05$	4.41	0.77	$12.55^{d} \pm 0.17$	9.47	0.75	$3.05^{f} \pm 0.10^{f}$	2.25	0.74
	El-Nobaria (Abdel-Wahab)	$5.10 {}^{\rm f} \pm 0.18$	3.67	0.72	$8.00\ ^{e}\pm0.15$	5.76	0.72	$3.72 \ ^{\rm f} \pm 0.10$	2.72	0.73
	Al-Hawia	$13.16 \ ^{d} \pm 0.21$	9.89	0.75	$4.53^{\ g}\pm0.12$	3.70	0.82	$6.91 \ ^{e} \pm 0.22$	4.99	0.72
Groundwater	Abdel-Rahman	6.84 ^e ± 0.16	5.30	0.77	$12.33^{d} \pm 0.12$	9.96	0.81	$7.15^{e} \pm 0.19$	4.82	0.67
Contaminated	Kafr-Dokhmais	40.04 ^a ± 0.32	32.7	0.82	$44.29^{b}\pm 0.16$	39.43	0.89	29.82 $^{b} \pm 0.27$	24.57	0.82
effluents	Al-Nasiria	$33.77 \ ^{b} \pm 0.26$	26.75	0.79	$59.27 \text{ a} \pm 0.23$	49.36	0.83	41.58 ^a ± 0.34	30.59	0.74
Contaminated water by sewage	Kafr Hakem	34.37 ^b ± 0.36	29.25	0.85	$14.25 ^{\text{c}} \pm 0.10$	12.03	0.84	15.67 ° ± 0.32	13.34	0.85
	Abu-Roash	$21.74 \ ^{c} \pm 0.34$	18.98	0.87	$44.58^{\ b} \pm 0.14$	38.32	0.86	41.27 ^a ± 0.24	32.29	0.78
LSD		0.736			0.483			0.699		

Table 3. Concentrations of copper, nickel and chromium in the soil and its bioaccumulation in maize

*BF: Bioaccumulation factor. Means followed by different subscripts within column are significantly different at the 5% level.

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The total uptake, consequently the BF values, of heavy metals by maize was increased with the decrease of pH values in soils with the same texture. For example, clay loamy soils of Kafr-Dokhmais and Al-Nasiria with the pH values of 8.29 and 8.48 had BF values of 93 and 88, respectively for Pb and 92 and 88 for Cd (Tables 1 and 2). Also, the same manner was observed with the soils of loamy sand texture. These findings confirmed the observations of Garciia et al. [46]; Wang et al. [47]; Khan et al. [48] who stated that heavy metals' bioavailability, like Cu and Zn, showed a significantly negative correlation with the soil pH. Wang et al. [49] reported that the metal solubility was greatly increased as the pH decreased; consequently, lowering the pH had significantly enhanced the plant metal uptake.

It was worthy to mention that BF values of heavy metals varied between the studied soils, where the wastewater-irrigated soil showed BF averages at the following descending order: Pb > Cd > Ni > Cu > Cr. Meanwhile, the Nile or groundwater-irrigated soils exhibited BF values arranged as Cu = Ni > Cr > Cd > Pb. These differences in heavy metals BF values may the interaction be related to between the physicochemical characteristics, the metal availability [50], and the metal binding capacity to roots [51]. In this respect, the obtained data confirmed the results of Lu et al. [17] who found that the BF values for heavy metals (Pb, Cr, Ni and Zn) in maize were all less than 1, which indicated lower concentrations of heavy metals in maize organs.

3.4. Distribution patterns of heavy metals in maize parts associated with the progressive uptake from the soil

Figures 1 and 2 clarified the distribution pattern for each element of the studied heavy metals. Part (A) of each figure represented the ratios of the element contents in each maize part as averages of the 9 sites under investigation, while part (B) of the figure showed the distribution of the element between the different parts of maize plant through the ascending order of the total content of the element in maize.

It was worthy to state that all the studied heavy metals showed similar distribution patterns through the maize parts, where the majority of heavy metals were retained in the root followed by leaves then the stem. On the other hand, the cob and grains contained the lowest concentrations of all elements. Figures of the average ratios (part A) revealed that maize grains contained the lowest ratios of all elements; 2% of Cr (Fig. 2), 5% of Cd and Ni (Fig. 1 and 2), and 7-8% of Pb and Cu (Fig. 1 and 2). Additionally, the cob had 5-11% of heavy metals. Meanwhile, the stem, leaves and root contained (16-19%), (21-27%) and (36-55%), respectively of the 5 heavy metals under investigation. Thus, the retention of heavy metals in maize organs can be arranged in a descending order as follows: roots > leaves > stem > cob > grains. These findings were in agreement with Van Assche and Clijsters [52], Angelova et al. [53] and Khan et al. [48] who revealed that heavy metal concentrations varied in the different parts of the same plant. As well, the root concentrations were higher than shoot (as reported by Rizwan et al. [54]), while the fruit was characterized as a low-rate accumulation part in the plant as confirmed by Verma and Dubey [55] as well as Seleiman and Kheir [34]. Lu et al. [17] reported similar findings to the obtained results concerning the distribution patterns of heavy metals (Pb, Cr and Ni) in maize organs, wherein the metals concentration decreased in the following order: roots > leaves > stem > grains.

3.5. Heavy metals level in maize grains as compared to the FAO/WHO permissible limits

Data of Table (4) showed the detected concentrations of heavy metals in maize grain samples as compared to the assigned MRLs by FAO/WHO. It was worthy to mention that all the studied heavy metals were detected in samples of maize cultivated in the soils irrigated by industrial effluents and sewage wastewater. This high incidence could be related to the high heavy metals content in that wastewater. However, all detected concentrations of toxic metals in maize grains located within the safe limits as compared to the MRLs except for Ni in samples of Kafr-Dokhmais, Al-Nasiria and Abu-Roash (soils irrigated with the polluted water) which were \geq the MRLs. The results presented in Table (4) were relatively similar to those of Mirecki et al. [40] who detected Pb, Cd and Cu in maize grains cultivated in polluted and non-polluted soils as (0.06, 0.01 and 2.76) and (0.05, 0.01 and 0.40) (mg kg⁻¹), respectively. Also, Angelova et al. [53] found that the translocation rate of heavy metals to the fruit was rather low in the fruiting vegetables.



Figure 1. Uptake and distribution of Pb and Cd in maize parts; A: Ratios of the element in maize parts (averages of the 9 studied sites). B: distribution of the element in maize parts (root, stem, leaves, cob and grain) of 9 sites based on the ascending of the element concentration.

Source of irrigation water	Site	Pb	Cd	Cu	Ni	Cr
	Wadi El-Natron	0.00	0.009	0.50	0.14	0.12
NT'I	El-Nobaria (Abdel-Rakib)	0.04	0.000	0.28	0.51	0.00
Nile river water	El-Nobaria (Abdel-Wahab)	0.00	0.000	0.23	0.23	0.00
	Al-Hawia	0.03	0.010	0.71	0.18	0.15
Groundwater	Abdel-Rahman	0.00	0.000	0.42	0.49	0.00
To Janda's La COlassa da	Kafr-Dokhmais	0.55	0.076	2.73	1.63	0.79
Industrial effluents	Al-Nasiria	0.52	0.112	1.77	2.06	0.50
	Kafr Hakem	0.26	0.038	2.51	0.81	0.47
Sewage wastewater	Abu-Roash	0.39	0.063	1.69	1.57	0.66
MRL (FAO/WHO)		2.00	1.00	30.00	1.50	1.30



Figure 2. Uptake and distribution of Cu, Ni and Cr in maize parts; A: Ratios of the element in maize parts (averages of the 9 studied sites). B: distribution of the element in maize parts (root, stem, leaves, cob and grain) of 9 sites based on the ascending of the element concentration.

3.6. Risk assessment of exposure to heavy metals through maize grains

The hazard quotient (HQ) of the maize grains for human consumption at different levels of the detected heavy metals was shown in Table (5). The HQ values of Pb and Cr were higher than other elements. The rank order of HQ was Cd > Pb > Ni > Cu > Cr. However, all HQ values which calculated using the lowest, average and highest detected concentrations were lower than 0.4 (0.0 - 0.34). This means that low potential risk is expected for adult people who could consume the highly contaminated maize from Kafr-Dokhmais and Al-Nasiria sites (Table 4).

Heavy metals	TDI* (µg/70 kg adult person/day)	EDI** (µg	;)		HQ***	HQ***			
		Lowest conc.	Mean conc.	Higher conc.	Lowest conc.	Mean conc.	Higher conc.		
Pb	252	3.19	31.68	58.41	0.013	0.126	0.232		
Cd	35	0.96	5.45	11.89	0.027	0.156	0.340		
Cu	35000	24.43	127.91	289.93	0.001	0.004	0.008		
Ni	3500	14.87	89.92	218.77	0.004	0.026	0.063		
Cr	105000	12.74	47.61	83.90	0.000	0.000	0.001		

Table 5. Risk assessment for heavy metals in maize grains

*TDI: Tolerable daily intake, **EDI: Estimated daily intake, ***HQ: Hazard quotient

4. Conclusion

Eventually, the results indicated that Ni, Cu and Cr were the most abundant elements detected in the studied soil sites followed by Pb and Cd. As well, Pb and Cd levels in soils irrigated with contaminated water by industrial effluents or sewage were 2 or 3 times greater than the levels of soils irrigated by the Nile and ground waters. However, Cu, Ni, and Cr levels of contaminated-water irrigated soils were 3.75-4.90 times greater than of those of fresh-water irrigated soils. Values of heavy metals total uptake by maize from the soils irrigated by wastewater were 3.3-5.6 folds of those soils irrigated by fresh water. Soils irrigated with wastewater showed BF averages for heavy metals at the following descending order: Pb > Cd > Ni > Cu > Cr. Meanwhile, soils irrigated by the Nile or groundwater exhibited BF values which can be arranged as Cu = Ni > Cr > Cd > Pb. The translocation of heavy metals was found to be accumulated in maize organs as the following order: roots > leaves > stem > cob > grains. It is worth noting that when concentrations of heavy metals were increased in the soil, the excess amounts of the absorbed metals were accumulated greatly in the roots, leaves, and then stems. Meanwhile the accumulated quantities of heavy metals were not significantly increased in grains. In addition, except for Ni of maize grains from soils irrigated with the polluted water, all the detected amounts of heavy metals in maize grains were satisfactory located within the recommended permissible limits by FAO/WHO. Moreover, low potential risk for public health was found, when calculating hazard quotient of the maize grains for human consumption at

5. Acknowledgement

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6. Declaration of competing interests

The authors declare that there are no conflicts of interest between them.

7. References

- Guo, G. L., & Zhou, Q. X. (2006). Evaluation of heavy metal contamination in Phaeozem of northeast China. *Environmental Geochemistry and Health*, 28(4), 331-340.
- (2). Ahmed, M. B. M., Rajapaksha, A. U., Lim, J. E., Vu, N. T., Kim, I. S., Kang, H. M., Lee, S.S. & Ok, Y. S. (2015).

different levels of the detected heavy metals. Therefore, it can be concluded from the current study that maize grains grown in soils with either low or high contents of heavy metals was safe. Additionally, the cob part of maize, which showed low heavy metals content, can be converted to biochar to be applied to the contaminated soil for the remediation purposes. Moreover, the high retention of heavy metals in maize's root, stem and leaves can nominate maize as a potential accumulator plant and can serve as an ideal remediation plant. The present investigation has a complementary stage of research which will focus on the biological and physical remediation of heavy metals-contaminated soils, and the different proposed remediation methods will be evaluated by maize cultivation in the treated soils.

Distribution and accumulative pattern of tetracyclines and sulfonamides in edible vegetables of cucumber, tomato, and lettuce. *Journal of Agricultural and Food Chemistry*, *63*(2), 398-405.

- (3). Liu, R., Wang, M., Chen, W., & Peng, C. (2016). Spatial pattern of heavy metals accumulation risk in urban soils of Beijing and its influencing factors. *Environmental Pollution*, 210, 174–181.
- (4). Jimenez-Ballesta, R., Garcia-Navarro, F., Bravo, S., Amoros, J., Perez-de-los-eyes, C., & Mejias, M. (2017). Environmental assessment of potential toxic trace element contents in the inundated floodplain area of Tablas de Daimiel wetland (Spain). *Environmental Geochemistry and Health*, 39, 1159–1177.
- (5). Devi, N. L., & Yadav, I. C. (2018). Chemometric evaluation of heavy metal pollutions in Patna region of the Ganges alluvial plain, India: implication for source apportionment and health risk assessment. *Environmental Geochemistry and Health*, 1-16.
- (6). Toth, G.; Hermann, T.; Da Silva, M. R. & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International*, 88, 299-309.
- (7). Abdel-Rahman, G. N., Ahmed, M. B. M., Saleh, E. M., & Fouzy, A. S. M. (2018). Estimated heavy metal residues in Egyptian vegetables in comparison with previous studies and the recommended tolerable limits. *Journal of Biological Sciences*, 18(3), 135-143.
- (8). Abdel-Rahman, G. N., Ahmed, M. B. M., Sabry, B. A., & Ali, S. S. (2019). Heavy metals content in some nonalcoholic beverages (carbonated drinks, flavored yogurt drinks, and juice drinks) of the Egyptian markets. *Toxicology reports*, 6, 210-214.
- (9). Shi, H. (2013). Heavy metal toxicity and therapeutics. Journal of Drug Metabolism and Toxicology, 4(5): e120. doi:10.4172/2157-7609.1000e120.
- (10). Aksoy, A.; Celik, A., Ozturk, M. & Tulu, M. (2000). Roadside plants as possible indicators of heavy metal pollution in Turkey. *Chemia i Inżynieria Ekologiczna*, 7 (10): 991-996.
- (11). Voutsa, D.; Grimanis, A. & Samara, C. (1996). Trace elements in vegetables grown in industrial areas in relation to soil and air particulate matter. *Environmental Pollution*, 94(3), 325-335.
- (12). Powlson, D. S. (1997). Integrating Agricultural Nutrient Management with Environmental Objective: Current State and Future Prospects. Proceedings of the Fertiliser Society, International Fertilizer Society, York.
- (13). Wangstrand, H.; Eriksson, J. & Oborn, I. (2007). Cadmium concentration in winter wheat as affected by nitrogen fertilization. *European Journal of Agronomy*, 26, 209-214.
- (14). Chandrasekaran, B.; Annadura, K. & Somasundaram, E. (2010). Nutrient management "A Textbook of Agronomy", pp.548. Published by New Age International (P) Ltd., Publishers.
- (15). Hafez, E. M., & Abdelaal, K. A. (2015). Impact of nitrogen fertilization levels on morphophysiological characters and yield quality of some maize hybrids (*Zea mays L.*). *Egyptian Journal of Agronomy*, 37(1): 35-48.
- (16). Opaluwa, O. D.; Aremu, M. O., Ogbo, L. O., Abiola, K. A., Odiba, I. E., Abubakar, M. M. & Nweze, N. O. (2012). Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. Advances in Applied Science Research, 3 (2):780-784.
- (17). Lu, Y., Yao, H., Shan, D., Jiang, Y., Zhang, S., & Yang, J. (2015). Heavy metal residues in soil and accumulation in

Egypt. J. Chem. 65, No. 9 (2022)

maize at long-term wastewater irrigation area in Tongliao, China. Journal of Chemistry, 2015, 1-9.

- (18). Klute, A. (1986). Methods of Soil Analysis. Part I: Physical and Mineralogical Methods. (2nd Ed), Amer. Soc. Agron. Monogragh No. 9, Madison, Wisconsin. USA.
- (19). Page, A. L.; Miller, R. H. & Keeny, D. R. (1982). Methods of Soil Analysis. Part II: Chemical and Microbiological Properties. (2nd Ed), Amer. Soc. Agron. Monogragh No. 9, Madison, Wisconsin. USA.
- (20). Jackson, M. L. (2005). *Soil chemical analysis: Advanced course*. UW-Madison Libraries Parallel Press.
- (21). Briscoe, M. (2015). Determination of Heavy Metals in Food by Inductively Coupled Plasma–Mass Spectrometry: First Action 2015.01. *Journal of AOAC International*, 98(4), 1113-1120.
- (22). Allen, S. E., Grimshaw, H. M., Parkinson, J. A., & Quarmby, C. (1974). *Chemical analysis of ecological materials*. Blackwell Scientific Publications, London.
- (23). APHA (2017). (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation). Standard Methods for the Examination of Water and Wastewater, 23rd ed. (Rice, E. W., Baird, R. B., Eaton, A. D., Clesceri, L. S. eds.) Washington DC.
- (24). Brooks, R. R. (1998). Plants that hyperaccumulate heavy metals, (CAB International: London, UK).
- (25). WHO (2003). GEMS/Food regional diets: regional per capita consumption of raw and semi-processed agricultural commodities. In *GEMS/Food regional diets: regional per capita consumption of raw and semi-processed agricultural commodities*. World Health Organization: Geneva, Switzerland. Available from: http://www.who.int/foodsafety/chem/gems_regional_diet.pdf (Accessed: December 15, 2020).
- (26). FAO/WHO (2001). Joint FAO/WHO. Food Standards Programme, 2-7 July, 2001, Codex Alimentarius Commission, Twenty-Fourth Session, Geneva, Switzerland.
- (27). Baars, A. J., Theelen, R. M. C., Janssen, P. J. C. M., Hesse, J. M., van Apeldoorn, M. E., Meijerink, M. C. M., ... & Zeilmaker, M. J. (2001). Re-evaluation of human-toxicological maximum permissible risk levels. RIVM Rapport 711701025. Available from: https://rivm.openrepository.com/rivm/bitstream/10029/9662/1/7117 01025.pdf. (Accessed: December 15, 2020).
- (28). EPA (2012). Quantitative risk assessment calculations. Sustainable futures/P2 framework manual 2012 EPA-748-B12-001 13. Quantitative Risk Assessment Calculations, 13, 1-11.
- (29). SAS (1999). Statistical Analysis System, SAS / STAT User's Guide. Release 6.03 Edn. SAS Institute, Cary, NC, 1028 PP.
- (30). Abuzaid, A. S. (2018). Soil quality indicators in Al-Qalyubia governorate as affected by long-term wastewater irrigation. *Egyptian Journal of Soil Science*, 58(1), 1-11.
- (31). Oladejo, N. A.; Anegbe, B. & Adeniyi, O. (2017). Accumulation of heavy metals in soil and maize plant (*Zea mays*) in the vicinity of two government approved dumpsites in Benin City, Nigeria. *Asian Journal of Chemical Sciences*, 3(3): 1-9.
- (32). Abou-Shanab, R. A., Ghozlan, H. A., Ghanem, K. M., & Moawad, H. A. (2007). Heavy Metals in Soils and Plants from Various Metal-Contaminated Sites in Egypt. *Terrestrial* and Aquatic Environmental Toxicology, 1(1), 7-12.
- (33). Mahmoud, E. K., & Ghoneim, A. M. (2016). Effect of polluted water on soil and plant contamination by heavy metals in El-Mahla El-Kobra, Egypt. *Solid Earth*, 7(2), 703-711.

- (34). Seleiman, M. F., & Kheir, A. M. (2018). Maize productivity, heavy metals uptake and their availability in contaminated clay and sandy alkaline soils as affected by inorganic and organic amendments. *Chemosphere*, 204, 514-522.
- (35). Dahnke, W., & Whitney, D. (1988). Measurement of soil salinity. Recommended Chemical Soil Test Procedures for the North Central Region, 221, 32–34.
- (36). Smith, J., & Doran, J. (1996). Measurement and use of pH and electrical conductivity for soil quality analysis. In *Methods for assessing soil quality* (Vol. 49). Soil Science Society of America Madison, WI.
- (37). Khaskhoussy, K., Hachicha, M., Kahlaoui, B., Messoudi-Nefzi, B., Rejeb, A., Jouzdan, O., & Arselan, A. (2013). Effect of treated wastewater on Soil and Corn Crop in the Tunisian Area. *Journal of Applied Sciences Research*, 9(1), 132-140.
- (38). Mollahoseini, H. (2013). Long term effects of municipal wastewater irrigation on some properties of a semiarid region soil of Iran. *International Journal of Agronomy and Plant Production*, 4(5), 1023-1028.
- (39). Eid, H. M. (2018). Amelioration of degraded soils irrigated with low quality water. M.Sc. Thesis, Department of Soil, Fac. Agric., Cairo Univ., Egypt, 125 p.
- (40). Mirecki, N., Agic, R., Sunic, L., Milenkovic, L., & Ilic, S. (2015). Transfer factor as indicator of heavy metals content in plants. *Fresenius Environmental Bulletin*, 24(11c), 4212-4219.
- (41). Chen, Z. S., Lee, D. Y., Wong, D., & Wang, Y. P. (1992). Effect of various treatments on the uptake of Cd from polluted soils by vegetable crops. In *Proceedings of 3rd Workshop of Soil Pollution and Prevention. National Chung-Hsing University, Taiwan ROC* (pp. 277-292).
- (42). El-Gendi, S. A., Badawy, S. H., & Helal, M. I. (1997). Mobility of some heavy metal nutrients in sandy soils irrigated with sewage effluent. *Journal of Agricultural Science - Mansoura University*, 22, 3535-3552.
- (43). Yang, Y., Zhang, F. S., Li, H. F., & Jiang, R. F. (2009). Accumulation of cadmium in the edible parts of six vegetable species grown in Cd-contaminated soils. *Journal of Environmental Management*, 90(2), 1117-1122.
- (44). Chaves, L. H. G., Estrela, M. A., & de Souza, R. S. (2011). Effect on plant growth and heavy metal accumulation by sunflower. *Journal of Phytology*, 3(12):04–09.
- (45). Aremu, M. O., Atolaiye, B. O., & Labaran, L. (2010). Environmental implication of metal concentrations in soil, plant foods and pond in area around the Derelict Udege mines of Nasarawa State, Nigeria. *Bulletin of the Chemical Society of Ethiopia*, 24(3), 351-360.
- (46). Garciia, I., Diez, M., Martíin, F., Simóon, M., & Dorronsoro, C. (2009). Mobility of arsenic and heavy metals in a sandyloam textured and carbonated soil. *Pedosphere*, 19(2), 166-175.
- (47). Wang, C., Yang, Z., Yuan, X., Browne, P., Chen, L., & Ji, J. (2013). The influences of soil properties on Cu and Zn availability in soil and their transfer to wheat (*Triticum aestivum* L.) in the Yangtze River delta region, China. *Geoderma*, 193-194, 131-139.
- (48). Khan, A., Khan, S., Khan, M. A., Qamar, Z., & Waqas, M. (2015). The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review. *Environmental Science and Pollution Research*, 22(18), 13772-13799.
- (49). Wang, A. S., Angle, J. S., Chaney, R. L., Delorme, T. A., & Reeves, R. D. (2006). Soil pH effects on uptake of Cd and Zn by *Thlaspi caerulescens*. *Plant and Soil*, 281(1-2), 325-337.

- (50). Bose, S., & Bhattacharyya, A. K. (2008). Heavy metal accumulation in wheat plant grown in soil amended with industrial sludge. *Chemosphere*, *70*(7), 1264-1272.
- (51). Toth, T., Tomáš, J., Lazor, P., BaJčan, D., & Jomova, K. (2009). The transfer of heavy metals from contaminated soils into agricultural plants in High Tatras region. *Czech Journal* of Food Sciences, 27, 390-393.
- (52). Van Assche, F., & Clijsters, H. (1990). Effects of metals on enzyme activity in plants. *Plant, Cell & Environment*, 13(3), 195-206.
- (53). Angelova, V. R., Babrikov, T. D., & Ivanov, K. I. (2009). Bioaccumulation and distribution of lead, zinc, and cadmium in crops of Solanaceae family. *Communications in Soil Science and Plant Analysis*, 40(13-14), 2248-2263.
- (54). Rizwan, M., Ali, S., Qayyum, M. F., Ok, Y. S., Zia-ur-Rehman, M., Abbas, Z., & Hannan, F. (2017). Use of maize (*Zea mays L.*) for phytomanagement of Cd-contaminated soils: a critical review. *Environmental Geochemistry and Health*, 39(2), 259-277.
- (55). Verma, S., & Dubey, R. S. (2003). Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants. *Plant Science*, 164(4), 645-655.