

# The effect of industrial activities on the heavy metals contamination of irrigation waters, soils, and plants in Kafr El-Dawar district, Egypt

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## **abstract**

The aim of this research was to evaluate the effect of industrial activities on the heavy metal contamination of irrigation water, soils, and plants in Kafr El-Dawar district, Egypt. An environmental monitoring of the pollution sources carried out in the study area through collection and analyses of water, soils, and plant samples in the representative locations. The results revealed that: (a) The qualities of all measured parameters of the fresh Mahmoudia canal water were within the recommended limits; (b) The amounts of heavy metals in Kafr El-Dawar drain water before receiving the outlet effluents of industrial companies ranged from 3 to 4 times higher than those in Mahmoudia canal; (c) The concentrations of heavy metals in the industrial outlet waste effluents for all studied companies were much higher than the permissible limits; (d) The concentrations of heavy metals at the mixing points between the industrial waste effluents and Kafr El-Dawar drain water were relatively low than that of the industrial outlet waste effluents, but still very high compared to that of Kafr El-Dawar drain water and permissible limits; (e) Heavy metals contents in soils adjacent to industrial companies were very high compared with that irrigated from Mahmoudia canal; (f) Soils adjacent to Textile and Spinning Company had toxic level of Cd, while the soils adjacent to Tinting and Chemicals, Industrial Silk Egyptian, and Al-Bayda Dyers Companies had toxic level of Pb, Cd, and Zn; g) The grown plants in Textile and Spinning soil had toxic level of Ni, plants grown in Tinting and Chemicals and Al-Bayda Dyers soils suffer from Pb, Ni, and Co toxicity, while the growing plants in industrial Silk soil suffer from Pb and Ni toxicity.

*Keywords:* Contamination, Industrial Wastewater, Lead, Cadmium, Nickel, Cobalt, Zinc

## **1. Introduction**

The main sources of water pollution are industrial, agricultural, and municipal wastewater, landfill leachate, runoff from the farmlands and the urban areas [1]. Heavy metals are the large group of elements having densities greater than 5 g·cm–3 [2]. Examples are Cd, Ni. Pb, Cr. Co. Hg, Cu and Zn. Unlike organic contaminants, which are eventually decayed to  $CO_2$  and  $H_2O$ , heavy metals are difficult to degrade once released into the ecosystem. Heavy metals are bound to sediments and soils and resist in the ecosystem till mobilized by changes in hydrogeology, vegetation,

or weather conditions [3]. Water pollution by heavy metals is considered one of the severe hazards to mankind's health [4]. Heavy metals get in the ecosystem as non-degradable and highly stable pollutants [5], causing contamination for both groundwater and surface resources. Decreasing water supplies and the increasing need for water combined with contamination activities elucidates the significance of water quality monitoring [6]. The attention is more earnest in semi-arid and arid countries where there is a lack of water and crop production depends mainly on irrigation.

The water contamination by heavy metals affects all organisms. Humans are more susceptible to serious health

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troubles because the heavy metal concentrations increase in the food chain [7]. The human toxicity potential of selected heavy metals follows the order Hg > Cd > Cu > Zn > Ni > Pb > Cr > Al > Co [8]. The level of toxicity depends on the rate of emission, dosage, and period of exposure. Heavy metals exposure has been linked to skin, lung, liver, kidney, bladder cancer [9] as well as cardiovascular disease [10]. Industrial wastewater may contain heavy metals. Human exposure to polluted wastewater is common, particularly where wastewater is reused for agricultural purposes or in the densely populated urban areas. In several countries around the world, the efficient of wastewater reuse is a great challenge [11]. Aris et al. [12] reported that different factories caused the increased levels of Fe, Al, Zn, Cr, Ni, Cu, Pb, Mn and Sn close to Langat River. The discharges of industrial effluent produce raised water contamination [13,14]. Irrigation with polluted waters led to an increase in heavy metal contents in soil and cultivated crops [15]. A strong correlation was observed between the level of heavy metals in soil, irrigated with contaminated water, and the levels of these metals in the leaves of cultivated crops.

Kafr El-Dawar district, El Beheira Governorate, Egypt, is an agricultural area, but with extensive industrial activities. It contains four major industrial companies, that is, Textile and Spinning Egyptian (T&S), Tinting and Chemicals (T&C), Industrial Silk Egyptian (IS), and Al-Bayda Dyers (BD) companies are located from a south to north direction. These companies unfortunately have been using the agriculture drainage system to dispose their waste effluents, which in most cases contain heavy metals. Kafr El-Dawar agriculture soils suffer from a shortage in irrigation water resources as a general case in north Egypt. Agricultural drainage water is currently being utilized as a main or supplementary source of irrigation water in this area. The use of such polluted water in soil irrigation raises the risk of contaminating soils with different industrial contaminants such as high-suspended materials and heavy metals. Therefore, the objective of the

present research concerned with the environmental monitoring of Kafr El-Dawar industrial area is to evaluate the effect of industrial activities on heavy metals contamination of irrigation water, soils, and growing plant.

#### **2. Materials and methods**

#### *2.1. Kafr El-Dawar industrial area samples*

to evaluate the effect of the industrial activities established therein on environmental contamination with some heavy metals, the samples of water, soils, and plant were collected from sites adjacent to four major industrial companies in Kafr El-Dawar area (i.e., Textile and Spinning Egyptian Company (T&S), Tinting and Chemicals Company (T&C), Industrial Silk Egyptian Company (IS), and Al-Bayda Dyers Company (BD)). The locations of these industrial companies are illustrated in Fig. 1.

#### *2.1.1. Water sampling*

Over 6 months from January to June, water samples were monthly collected from 10 sites on the drainage network adjacent to Industrial Kafr El-Dawar area. These sites representing either the locations where the companies dispose their liquid wastes in the industrial secondary drains, or the points at which Kafr El-Dawar drain and Abu-Qir drain receive industrial drainage waste effluent from each company. Samples sites are illustrated in Table 1 and Fig. 1.

#### *2.1.2. Soil and plant sampling*

Surface soil samples (0–30 cm) were collected from agricultural soils adjacent to each mentioned industrial company. Selected physical and chemical characteristics of tested soils are given in Table 5. Also, vegetative parts of growing plants (i.e., wheat, clover, and faba bean) at the time of study were taken for analysis.



Fig. 1. Water sampling sites on the drainage network adjacent to industrial Kafr El-Dawar area.





#### *2.2. Soil analysis*

The collected soil samples were air dried, ground with a wooden pestle, passed through a 2 mm sieve, and analyzed for different soil properties. Particle size analysis was determined by the hydrometer method [16]. Soil pH was measured in 1:2.5 soil: water suspension [17]. Electrical conductivity  $(EC_e)$  was measured in the saturated soil paste extract according to the study of Cottenie et al. [17]. Soluble cations and anions were determined in the saturated soil paste extract as described by the study of Page et al. [18]. Calcium carbonate equivalent (CCE) was estimated by the pressure-calcimeter method [19]. Soil organic matter (OM) was measured by the modified Walkley–Black method [20]. Available heavy metals were determined using DTPA-solution [21] and measured by ICP-OES. Total heavy metals were extracted by aqua regia and measured by ICP-OES [17].

## *2.3. Plant analysis*

The collected plant samples were washed with distilled water, air dried, and oven dried at 65°C for 48 h and ground in a mill. An acid digestion procedure was performed for the plant dried samples [22]. Heavy metals were measured using ICP-OES.

#### *2.4. Water analysis*

The water samples were taken from each site (about 2 L), bottled, tightly stoppered, and transferred to the laboratory for immediate chemical analysis, according to standard methods for examination of water and wastewater [23].

#### *2.5. Statistical analysis*

To test for statistical differences, an analysis of variance was calculated using PROC GLM followed by Student– Newman–Keuls (SNK) test for mean comparisons using SAS 9.4 statistical software [24]. A significance level of  $\alpha$  = 0.05 was chosen to reduce the likelihood of a Type II error in analysis of water, soil, and plant data.

Table 2

Recommended maximum concentration of studied heavy metals in irrigation water

Metal	Recommended maximum concentration <sup>a</sup>
Cadmium (Cd), $mg \cdot L^{-1}$	0.01
Cobalt (Co), $mg \cdot L^{-1}$	0.05
Nickel (Ni), $mg \cdot L^{-1}$	0.20
Zinc $(Zn)$ , mg·L <sup>-1</sup>	2.00
Lead (Pb), $mg \cdot L^{-1}$	5.00

*a* according to [25–30].

#### **3. Results and discussion**

## *3.1. Chemical analysis of irrigation water in the polluted area*

The average values obtained from water analysis are present in Table 3. All measured heavy metals were compared to the recommended guidelines (Table 2) [25–30]. These national and international guidelines were designed for long-term protection of soil and water resources, plants, animals, and humans.

#### *3.1.1. Mahmoudia canal water*

Data in Table 3 show the chemical analysis of Mahmoudia canal water (M.C.) (main source of irrigation water). Data indicated that all measured parameters are within the recommended limits for water irrigation according to recommended guidelines (Table 2). Data also showed that the concentrations of cations was in the following order:  $Na > Ca > Mg > K$ , and the anions was in the order  $SO_4^{-2} > Cl^- > HCO_3^- > CO_3^{-2}$ . With respect to SAR values, data indicated that this water could be used without any hazard to alkalinity.

#### *3.1.2. Kafr El-Dawar drain water*

Kafr El-Dawar agriculture soils suffer from a shortage in irrigation water resources as a general case in north Egypt.

Table 3

Chemical analysis of Mahmoudia canal water (M.C.), Kafr El-Dawar drain water (K.D.), the outlet effluents of industrial companies (1) and their mouth effluents discharge on agriculture drainage water (2)

Analyte	Units	M.C.	K.D.	T&S1	T&S2	T&C1	T&C2	IS1	IS <sub>2</sub>	B <sub>D</sub> 1	B <sub>D</sub> 2
pH		7.46 a	7.32a	7.05a	7.37 a	6.43 a	6.89a	6.91 a	7.27a	7.29a	7.21a
EC	$dS·m-1$	$0.53$ d	1.20c	1.23c	1.19c	2.38a	1.89 <sub>b</sub>	1.71 <sub>b</sub>	$1.42\,\mathrm{bc}$	1.89 b	1.62 <sub>bc</sub>
Ca	$meq·L^{-1}$	1.47c	2.7 <sub>b</sub>	2.67 <sub>b</sub>	2.74 <sub>b</sub>	4.04a	4.56a	4.15a	3.64a	4.01a	4.13a
Mg	$meq·L^{-1}$	1.30e	2.27d	2.31 <sub>d</sub>	2.32d	4.56a	3.89 <sub>b</sub>	3.36 bc	2.81 dc	3.57 bc	3.02 bcd
Na	$meq·L^{-1}$	2.68d	7.22c	9.37 bc	7.2 c	13.1a	11.54 ab	8.64 с	7.23c	9.21 bc	9.28 bc
K	$meq·L^{-1}$	0.07e	0.41 <sub>d</sub>	0.15e	0.11e	0.9a	0.78 <sub>b</sub>	0.15e	0.63c	0.12e	$0.44$ d
CO <sub>3</sub>	$meq·L^{-1}$	0.00 a	0.00a	0.00a	0.00a						
HCO <sub>3</sub>	$meq \cdot L^{-1}$	1.57 d	2.35c	2.91 bc	2.37c	4.06a	3.91 a	$3.29$ ab	2.72 bc	$3.32$ ab	3.91a
Cl	$meq·L^{-1}$	1.83 e	5.52 d	7.16 cd	5.92 cd	11.7 a	9.55 b	8.31 bc	6.73 cd	8.06 bc	7.68 bcd
SO <sub>4</sub>	$meq \cdot L^{-1}$	2.21 e	4.42 cd	4.38 cd	4.08 <sub>d</sub>	$6.05$ ab	6.71a	4.98 bcd	4.33 cd	5.53 abcd	5.74 abc
SAR		2.36d	4.58 bc	5.94 ab	4.53 bc	6.32a	5.61 ab	4.46 bc	4.03c	4.73 bc	4.91 bc
adjSAR		3.26 e	8.71 cd	11.81 bc	8.66 cd	14.94 a	12.96 ab	9.84 cd	8.37 d	10.46 bcd	10.62 bcd
<b>TSS</b>	$mg \cdot L^{-1}$	23.64 f	97 e	223 bc	326a	178 cd	249 b	197 bcd	231 bc	165 d	234 bc
<b>TDS</b>	$mg \cdot L^{-1}$	386 f	847 de	882 de	823 e	1432 a	1380 ab	1161 abcd	972 cde	1235 abc	1100 bcde
Cd	$mg \cdot L^{-1}$	0.005e	0.02e	0.13c	0.07 <sub>d</sub>	0.27a	0.16c	0.22 <sub>b</sub>	0.13c	0.16c	0.09 <sub>d</sub>
Zn	$mg \cdot L^{-1}$	0.31 f	0.86f	2.95 de	2.08 <sub>e</sub>	5.58 <sub>b</sub>	4.36 с	4.85 bc	2.41 e	6.79a	3.48 d
Ni	$mg \cdot L^{-1}$	0.07 <sub>d</sub>	0.19 <sub>d</sub>	0.97c	0.73c	1.96a	1.37 <sub>b</sub>	1.47 b	0.92c	1.51 <sub>b</sub>	1.03c
Pb	$mg \cdot L^{-1}$	0.13 <sub>d</sub>	$0.34$ d	0.72d	$0.42$ d	9.53a	7.11 b	8.21 b	5.43 с	7.53 b	5.09c
Co	$mg \cdot L^{-1}$	0.01e	$0.03$ de	0.02e	$0.03$ de	0.43a	0.15c	0.09d	$0.05$ de	0.41a	0.23 <sub>b</sub>

M.C.: Mahmoudia canal; K.D.: Kafr El-Dawar drain; T&S: Textile and Spinning Egyptian Company; T&C: Tinting and Chemicals Company; IS: Industrial Silk Egyptian Company; BD: Al-Bayda Dyers Company.

*a*Within columns, values followed by different lowercase letters are significantly different at  $\alpha$  = 0.05.

Reuse of lower quality of agricultural drainage water is increasing in this area as an alternative source for land irrigation. Data in Table 3 show the average values obtained for chemical analysis of Kafr El-Dawar drain (K.D.) before receiving the outlet effluents of industrial companies. Data indicated that salinity (EC) may affect the sensitive plants, but no specific ion effects of sodium or chloride on reducing crop production are expected. Also, the results in Table 3 indicate that no hazardous effect of SAR on soil physical properties such as permeability was expected. Except for cadmium, concentrations of measured heavy metals were lower than the critical limits (Table 2). It must be mentioned that heavy metals concentration ranged from three to four times higher than those in Mahmoudia canal water, this may be due to discharge of some municipal effluents or some herbicides to the drainage water.

## *3.1.3. Outlet effluents of industrial companies and their mouth effluents discharge on agriculture drainage water*

#### *3.1.3.1. Textile and Spinning Egyptian Company*

This company is located at 28 km south to Alexandria city. Two sampling sites (T&S1 and T&S2) were included, T&S1 represent the company outlet effluent discharge to the industrial secondary drain, while T&S2 represent the mixing point between the industrial secondary drain effluent and Kafr El-Dawar drain water (Fig. 1). Data in Table 3 show that EC values of each outlet effluent (T&S1) and mouth (T&S2) equal to that at the drain water (K.D.), while SAR value of outlet effluent (T&S1) was approximately caused alkalinity hazard to the soils, however, after mixing (T&S2), the SAR value decreased to the permissible limits. Data also indicated that Kafr El-Dawar drain water at mixing point (T&S2) was highly loaded by total suspended solids (TSS) which were higher in average by 103 mg·L<sup>-1</sup> than outlet effluent discharge (T&S1), this may be due to misuse of industrial effluent in the secondary drain for disposing of sewage water.

Except for Pb and Co, which is less than the permissible limits, other measured heavy metals in outlet effluent (T&S1) were higher than the safe limits. Kafr El-Dawar drain at mixing point (T&S2) was loaded with toxic level of Cd, Zn, and Ni, the expected amount of Cd, Zn, and Ni are 0.7, 20.8, and 7.3 kg·ha–1 per meter of applied water. Pratt and Suarez [31] reported that Cd concentration equal to or less than 0.01 mg·L–1 requires 50 y or more to exceed the recommended maximum cadmium-loading rate in soil.

#### *3.1.3.2. Tinting and Chemicals Company*

This Company is located at 2.75 km north to Misr Textile and Spinning Company. Two sampling sites (T&C1 and T&C2) were included, T&C1 represent the company outlet effluent discharge to the industrial secondary drain, while T&C2 represent the mixing point between the industrial secondary drain effluent and Abu-Qir drain water (Fig. 1). Data in Table 3 showed that the average values of pH during the period of study led to decrease the water

pH to acidity. All measured cations and anions were higher than those of the textile company. SAR recorded in outlet effluents (T&C1) was the highest value in all sites, associated with higher EC.

Heavy metals measurements revealed that the discharged effluents (T&C1) were loaded with toxic levels of all metals over the permissible limits (Tables 2 and 3). The measured parameters of tinting and chemicals discharge effluent pointed to their higher impact on the agricultural environment compared to textile discharge effluent. According to the reported data of discharged effluent of Tinting and Chemicals Company (T&C1), it expected that Abu-Qir drain water would have low quality at mixing sites (T&C2), as expected all parameters recorded the highest values in this site (T&C2). Despite the dilution effect of drain water, results showed that all studied heavy metals were above the permissible limits. The expected amounts of heavy metals that reach soils from reusing drainage water in this site (T&C2) were estimated by 1.6 kg·Cd·ha<sup>-1</sup> per meter of applied water for land irrigation. While the expected amount of Zn, Ni, Pb, and Co were 43.6, 13.7, 71.1, and 1.5 kg·ha–1 per meter of applied water for land irrigation, respectively. On the other hand, the permissible limits of irrigation water standard for Cd, Zn, Ni, Pb, and Co are 0.1, 20, 2, 50, and 0.5 kg·ha–1 per meter of applied water for land irrigation, respectively. The obtained results indicate that high rate of addition of Cd, Zn, Ni, Pb, and Co at toxic levels to the soils will deteriorate soil fertility and reduce soil productivity too on the long term.

## *3.1.3.3. Industrial Silk Egyptian Company*

This Company is located at 0.5 km north to Tinting and Chemicals Company. Two sampling sites (IS1 and IS2) were included, IS1 represent the company outlet effluent discharge to the industrial secondary drain, while IS2 represent the mixing point between the industrial secondary drain effluent and Abu-Qir drain water (Fig. 1). Data in Table 3 show that all measured parameters of outlet effluent discharge (IS1) have higher values than those of Kafr El-Dawar drain water (K.D.). All those parameters were decreased at (IS2) after mixing with drain water, but still above that of Kafr El-Dawar drain water (K.D.).

The reported values of heavy metals in Table 3 revealed that the effluent (IS1) was loaded with toxic levels of all studied heavy metals with respect to the permissible levels for land irrigation (Table 2). At the mixing point (IS2), data showed that the concentration of heavy metals were reduced to about half of those in the outlet effluent (IS1), but still, except for Co, higher than the permissible limits of the irrigation water standards. The expected addition rates of Cd, Zn, Ni, Pb, and Co to adjacent soils from reusing of drainage water were estimated by 1.3, 24.1, 9.2, 54.3, and 0.5 kg·ha–1 per meter of applied water for land irrigation, respectively. This expected addition rates of studied heavy metals to soils are lower than those closed to Tinting and Chemicals Company.

#### *3.1.3.4. Al-Bayda Dyers Company*

This Company is located at 23 km south to Alexandria city, and at 1.5 km north to Misr Synthetic Silk Company. Two sampling sites (BD1 and BD2) were included, BD1 represent the company outlet effluent discharge to the industrial secondary drain, while BD2 represent the mixing point between the industrial secondary drain effluent and Abu-Qir drain water (Fig. 1). Data in Table 3 show that the outlet effluent discharge (BD1), and the mixing point (BD2) have higher values of all measured parameters than Kafr El-Dawar drain (K.D.). Data also indicated that the outlet effluent (BD1) was loaded with toxic levels of all studied heavy metals. The average concentrations of measured heavy metals were 0.16, 6.79, 1.51, 7.53, and 0.41 mg·L<sup>-1</sup> of Cd, Zn, Pb, and Co, respectively. The above-mentioned values are much higher than the maximum recommended limit (Table 2) for long-term agricultural irrigation.

At the mixing point (BD2), measurements heavy metals revealed that the drain water were loaded with less toxic level of heavy metals compared to the industrial waste effluent (BD1). The average concentrations of studied heavy metals were 0.09, 3.48, 1.03, 5.09, and 0.23 mg·L<sup>-1</sup> of Cd, Zn, Pb, and Co, respectively. These values are still higher than the permissible limits. The expected amounts of added heavy metals to adjacent soils from reusing drainage water were 0.9, 43.8, 10.3, 50.9, and 2.3 kg·ha<sup>-1</sup> per meter of applied water of Cd, Zn, Pb, and Co, respectively.

Generally, heavy metals contents were varied between outlet and mouth of companies, but still very high compared to Kafr El-Dawar drain water (K.D.). Heavy metals contents of companies' outlet effluent discharge were arranged in the following orders: Tinting and Chemicals > Industrial Silk Egyptian > Al-Bayda Dyers > Textile and Spinning Egyptian companies for cadmium and lead, Tinting and Chemicals > Al-Bayda Dyers > Industrial Silk Egyptian > Textile and Spinning Egyptian companies for Zn, Ni, and Co. Low suitability of reused mixed drain water for long-term land irrigation will have an impact on the agricultural environment through soil fertility degradation and low soil productivity. Before reusing industrial wastewater, it should be treated to remove as many pollutants as possible. Wastewater treatment can mitigate the shortage of irrigation water in many countries and reduce pollutants entering aquatic ecosystems. A study conducted in Greece found that the treated wastewater, in Nafpaktos and Thermos, was contributed to 100% and 88% of the total irrigation water, respectively [32]. The same approach should be used in Kafr El-Dawar district to provide sufficient water for agricultural operations and reduce pollutants in industrial wastewater.

#### *3.2. Impact of industrial wastewater on the heavy metal contents of soils*

In industrial Kafr El-Dawar area, reused of drainage water mixed with industrial wastewater are frequently used for soil irrigation. According to the obtained data of drain network water analysis, the concentrations of heavy metals in soils adjacent to the industrial companies have the potential to be increased to toxic levels. Despite heavy metals are immobile in soils, there is a possibility to enter human food chain via edible parts of crops growing in the contaminated soils. The permissible limits of selected heavy metals according to Australia, Canada, China, Czech, Denmark, Finland, Italy, Lithuania, Malaysia, Norway, Poland, Slovakia, Sweden, Thailand, United Kingdom, and World Health Organization (WHO) [33–44] were recorded (Table 4). The guidelines of heavy metals in agricultural soils in Egypt were missing in the literature accessed (Table 4). Thus, the average permissible limits of selected heavy metals were used in this study as the standard limits of heavy metals in agricultural soils in Egypt (Table 4).

Data in Table 4 shows the total and available levels of heavy metals in soils next to the industrial companies, that is, T&S soil, T&C soil, IS soil, and BD soil, in addition of the control (M.C. soil, which irrigated with fresh water from Mahmoudia canal). It is noticed that there is a big difference between the two groups for each element, from one element to another, and from site to another. Depending on the nature, amount of each element, and the source of pollution. Data also indicated that the values of total and available heavy metals in soils adjacent to the industrial companies were very high compared to the reference soil (M.C. soil). The heavy metal levels in the studied area followed the decreasing order:  $Zn > Pb > Ni > Co > Cd$ .

The total content of Pb in soils close to the industrial companies (T&S, T&C, IS, and BD soils) varied widely from  $33.15$  to  $241.60$  mg·kg<sup>-1</sup> soil. These variations in Pb content from soil to another may be due to the considerable variations in the composition of different companies wastes. The highest value of total Pb were observed in the soil adjacent to Tinting and Chemicals Company (T&C soil), followed by that adjacent to Industrial Silk Egyptian Company (IS soil), then the soil adjacent to Al-Bayda Dyers Company (BD soil), while soil adjacent to Textile and Spinning

Egyptian Company (T&S soil) was the least affected. This may be due to the lower Pb content in the outlet and mouth of Textile and Spinning Company, while other companies produced high amounts of Pb in their outlet effluents discharge, which contribute to be high levels in soils close to these companies (T&C, IS, and BD soils).

Lead contents of the outlet effluents discharge of the different companies were arranged in the same descending order of that in soils adjacent to these companies, as follows: Tinting and Chemicals Company > Industrial Silk Egyptian Company > Al-Bayda Dyers Company > Textile and Spinning Egyptian Company. Comparing the obtained values of total Pb in soils adjacent to industrial companies (T&S, T&C, IS, and BD soils) with control (M.C. soil, which irrigated from Mahmoudia canal, and contains 25.5 mg·kg–1 soil), it is noticed that T&C, IS, and BD soils contain very high concentrations of Pb. According to the standard limits, which reported in Table 4, the average critical values of total Pb in soils was 142 mg·kg–1 soil, plant toxicity of Pb is possible in T&C, IS, and BD soils. The available Pb in soils showed the same trend of total Pb and has the same order of that of total Pb content in soils adjacent to industrial companies. It must be mentioned that available Pb contents, in both T&C, and IS soils, were as high as 25–30 times of that in the control (M.C. soil). This content of Pb may affect in plants growth.

Data in Table 5 indicate that total Ni content in soils adjacent to the industrial companies (T&S, T&C, IS, and BD soils) varied widely from 53.61 to 88.30 mg·kg–1 soil. The highest amount of total Ni was observed in T&C soil, followed by IS and BD soils, while T&S soil was the least contaminated

Table 4

Guidelines for the maximum permissible limit values of selected heavy metals in agricultural soil for various countries

References	Country		Maximum permissible level in soils (mg·kg <sup>-1</sup> )				
		Cd	Co	Pb	Ni	Zn	
$[35]$	Australia	3	50	600	60	200	
$[36]$	Canada	$1 - 1.2$	$19 - 22$	$45 - 120$	$37 - 130$	290-340	
$[37]$	China	0.6	$\qquad \qquad -$	350	60	300	
$[38]$	Czech	0.5	30	60	50	120	
$[39]$	Denmark	0.5	-	40	30	500	
$[40]$	Finland	$\mathbf{1}$	20	60	50	200	
$[39]$	Italy	2	20	100	120	150	
$[39]$	Lithuania	3	30	100	75	300	
$[41]$	Malaysia	0.3	10	65	45	95	
$[42]$	Norway	3	—	60	50	100	
$[43]$	Poland	$\overline{4}$	20	100	100	300	
$[39]$	Slovakia	5	50	150	100	500	
$[42]$	Sweden	0.4		80	35	350	
$[41]$	Thailand	0.15	20	55	45	70	
$[34]$		$1 - 5$	$20 - 50$	$20 - 300$	$20 - 60$	100-300	
$[33]$	UK	3	$25 - 50$	100-400	100	70-400	
$[44]$	<b>WHO</b>	3	50	100	50	300	
	Minimum	0.15	10	40	30	70	
	Maximum	5	50	600	120	500	
	Average	$\overline{2}$	30	142	64	249	

Analyte	M.C. soil <sup>a</sup>	T&S soil	T&C soil	IS soil	BD soil
pH	7.75 a	7.80 a	8.05a	7.69 a	7.92 a
$EC_{\rho}$ , dS·m <sup>-1</sup>	1.64 b	3.61a	4.74a	4.28a	3.91a
$Ca^{2+}$ , meq $·L^{-1}$	7.0 <sub>b</sub>	13.5 a	16.9 a	14.7 a	14.0a
$Mg^{2+}$ , meq·L <sup>-1</sup>	5.7b	4.7 b	4.7 b	6.0 <sub>b</sub>	9.4a
$Na^+$ , meq $\cdot L^{-1}$	4.7 c	18.5 b	24.9 a	23.1a	$16.5\,\mathrm{b}$
$K^*$ , meq $\cdot L^{-1}$	0.6c	1.2 <sub>b</sub>	2.8a	0.6c	0.8c
$CO32$ , meq·L <sup>-1</sup>	0.0a	0.0a	0.0a	0.0a	0.0a
HCO <sub>3</sub>	5.9d	$18.0\,\mathrm{b}$	$14.0\;{\rm c}$	23.4a	13.4 с
$Cl^-$ , meq $\cdot L^{-1}$	2.7c	11.0 <sub>b</sub>	23.0a	14.0 b	23.4a
$SO42$ , meq·L <sup>-1</sup>	7.8 b	7.0 <sub>b</sub>	10.4a	5.3c	2.3 <sub>d</sub>
CCE, %	3.45 с	6.73a	$6.05$ ab	5.09 <sub>b</sub>	4.82 b
OM, %	2.07a	2.22a	2.02a	2.69a	2.56a
Sand, %	24.7	29.3	29.8	36.2	39.4
Silt, %	33.1	40.3	42.2	34.0	32.4
Clay, %	37.2	30.4	28.0	29.8	28.2
Texture	Clay loam	Clay loam	Clay loam	Clay loam	Clay loam
Total Pb, mg·kg <sup>-1</sup>	25.50 с	33.15 с	241.60 a	211.70 a	142.30 b
Avail <sup>b</sup> . Pb, mg·kg <sup>-1</sup>	1.16d	1.40 <sub>d</sub>	32.61 a	28.14 b	17.54 с
Total Ni, mg·kg <sup>-1</sup>	28.18 c	53.61 b	88.30 a	60.72 b	56.10 b
Avail. N, mg·kg <sup>-1</sup> i	0.56c	1.05 <sub>b</sub>	1.82a	1.63a	1.88a
Total Cd, mg·kg <sup>-1</sup>	1.12c	3.56 <sub>b</sub>	7.13 a	8.32 a	6.68a
Avail. Cd, mg·kg <sup>-1</sup>	0.05c	0.14c	0.46 <sub>b</sub>	0.57a	0.41 <sub>b</sub>
Total Zn, mg·kg <sup>-1</sup>	56.2 c	62.35 с	305.2 a	346.3 a	215.5 b
Avail. Zn, mg·kg <sup>-1</sup>	3.26d	4.98 d	27.34 a	19.94 b	10.50c
Total Co, mg·kg <sup>-1</sup>	5.40 с	15.60 b	20.40a	13.02 b	12.06 b
Avail. Co, mg·kg <sup>-1</sup>	0.10 <sub>d</sub>	0.23 <sub>b</sub>	0.32a	0.15c	0.20 <sub>b</sub>

Table 5 Selected chemical, physical characteristics, and heavy metals content of the studied soil samples

*a* M.C. soil: irrigated from Mahmoudia canal; T&S soil: adjacent to Textile and Spinning Egyptian Company; T&C soil: adjacent to Tinting and Chemicals Company; IS soil: adjacent to Industrial Silk Egyptian Company; BD soil: adjacent to Al-Bayda Dyers Company. *b* available concentration (DTPA-extractable).

by Ni. Although, total Ni content in soils adjacent to industrial companies were about 2–3-fold as much as that of M.C. soil, there is no soil toxicity of Ni is only expected in the T&C soils, according to guidelines for the maximum permissible limits (Table 4), the average critical level of total Ni in soils is 64 mg·kg–1 soil. The available content of Ni in soils ranged from  $0.56$  to  $1.88$  mg·kg<sup>-1</sup> soil, with the following order: BD soil > T&C soil > IS soil > T&S soil > M.C. soil.

Total Cd content in the tested soils ranged between 1.12 and 8.32 mg·kg–1 soil (Table 5). Where the maximum recommended level of Cd in soils is 2 mg·kg–1 soil, as set by the guidelines shown in Table 4. This means that all soils adjacent to industrial companies had total Cd content above the permissible limits. Data in Table 5 show that IS soil contained the highest amount of total Cd, followed by T&C and BD soils, while T&S soil was the least contaminated. The available Cd content in soils show the same manner of total Cd order, it ranged between 0.05 mg·kg–1 soil in M.C. soil to 0.57 mg·kg–1 soil in IS soil. Data of discharged wastes in Table 3 show that Cd content in companies' outlet was very high compared to that of Kafr El-Dawar drain water. High Cd concentration in soils adjacent to industrial companies is due to discharge from industrial processes.

The total content of Zn in soils adjacent to the industrial companies varied widely from  $62.35$  to  $346.3$  mg·kg<sup>-1</sup> soil. The highest value of total Zn was observed in the soil adjacent to Industrial Silk Egyptian Company (IS soil), followed by T&C soil, then the BD soil, while T&S soil was the least affected. This arrangement was similar to that of the total Cd. Comparing the obtained values of total Zn in soils adjacent to industrial companies with control (M.C. soil, which irrigated from Mahmoudia canal, and contains  $56.2 \text{ mg} \cdot \text{kg}^{-1}$ soil), it is noticed that T&C, IS, and BD soils contain very high concentrations of Zn. When compared to the maximum permissible limits of agricultural soil, the critical value of total Zn in soils was 249 mg·kg–1 soil (Table 4), toxicity of Zn for plant is possible in  $T\&C$  and IS soils. The available content of Zn in soils ranged from 3.26 to 27.34 mg·kg<sup>-1</sup> soil, with the following order: T&C soil > IS soil > BD  $soil > T&S soil > M.C. soil.$ 

Data in Table 5 indicate that total Co content in soils adjacent to the industrial companies varied widely from 12.06 to 20.40 mg·kg<sup>-1</sup> soil. The highest value of total Co was observed in T&C soil, followed descending by T&S and IS soils, respectively, while BD soil was the least contaminated. Although, total Co content in soils adjacent to industrial companies were about 2–4-folds as much as that of M.C. soil, no soil toxicity of Co is expected in these soils, according to the standard limits, which reported that the average permissible limit of total Co in soils was 30 mg·kg–1 soil. The available contents of Co in soils adjacent to industrial companies were as high as 1.5–3 times of that in M.C. soil, and ranged from 0.15 to 0.32 mg·kg<sup>-1</sup> soil, with the following order: T&C soil > T&S soil > BD soil > IS soil.

To display an obvious indicator of which of the heavy metals may pose the greatest environmental hazards, the fold above the soil permissible limits for each element at each location is showed in Fig. 2. Results revealed that Cd levels highly exceeded the average permissible limit, followed by Pb, Zn and Ni. The highest fold above the permissible limit for Cd and Zn were found at soil adjacent to IS company (4.2, 1.4-fold, respectively), whereas the highest fold above the permissible limit for Pb, and Ni were found at T&C soil (1.7, and 1.4-fold, respectively).



Fig. 2. Relative toxic effects of total heavy metals at different sampling sites, expressed as fold above average permissible limit of different heavy metals in agricultural soil.

Generally, heavy metals contents in soils adjacent to industrial companies varied widely from site to another, but still very high comparing to that of M.C. soil, which irrigated using the water of Mahmoudia canal. These high values of heavy metals would affect the grown plants in these areas either in growth or in their element concentrations in the different plant organs, which would affect the human and animal food chains. Cd, Pb, and Zn were the most serious metal pollutants in soil samples collected from the studied area. It was noticed that the average level of total heavy metals in the soil samples was between 29–92 times more than the average level of the same heavy metals in water samples. This suggested that polluted irrigation water can result in increasing the level of heavy metals in soils. Total heavy metals contents in the studied soils were arranged in the following orders: T&C soil > IS soil > BD soil > T&S soil > M.C. soil for lead, and nickel; IS soil > T&C soil > BD soil > T&S soil > M.C. soil for cadmium and zinc, while cobalt contents in the studied soils were arranged as follows: T&C soil > T&S soil > IS soil > BD soil > M.C. soil.

## *3.3. Heavy metals contents in some plants grown in the tested polluted soils*

The contents of tested heavy metals in some growing plants are reported in Table 6. The values of tested heavy metals differ from site to another, and from plant to another. The relative differences in the uptake of metal ions among plant species and cultivars, it may be due to different factors, such as the rate of evapotranspiration, root exudates, surface area of the root, and root CEC [33].

Data in Table 6 indicate that heavy metals contents in plants grown in the soils adjacent to industrial companies (T&S, T&C, IS, and BD soils) were very high compared to that of M.C. soil, which irrigated from Mahmoudia canal. The obtained data of soils and plants show the positive

Table 6

Heavy metals contents (mg·kg<sup>-1</sup> dry matter) in some plants grown in the tested polluted soils.

Crop <sup>a</sup>	Heavy metals $mg \cdot kg^{-1}$	M.C. soil	T&S soil	T&C soil	IS soil	BD soil
	Pb	13.7 c	-	68.6 a	-	42.4 b
	Cd	$ND^b b$	-	3.1a	-	2.8a
Wheat	Ni	9.3c	-	26.4a	—	21.3 <sub>b</sub>
	Co	3.7 <sub>b</sub>		14.1 a	—	15.6a
	Zn	9.8 b		28.3a		28.6a
	Pb	11.7 d	15.6 d	76.6 a	38.0c	52.0 <sub>b</sub>
Clover	Cd	ND e	0.5d	3.7a	1.7c	2.2 <sub>b</sub>
	Ni	7.2 d	15.3c	38.3a	19.3c	30.4 <sub>b</sub>
	Co	4.4c	10.3 <sub>b</sub>	18.4a	12.8 <sub>b</sub>	13.5 <sub>b</sub>
	Zn	11.3c	17.5c	53.2a	28.4 b	28.2 <sub>b</sub>
Faba bean	Pb	19.3 <sub>b</sub>	21.3 <sub>b</sub>		56.4a	
	Cd	0.2c	0.6 <sub>b</sub>		1.3a	-
	Ni	8.1 b	12.8a		12.4a	
	Co	3.9 <sub>b</sub>	9.8a		10.5a	
	Zn	14.5 b	21.6a		25.4a	-

*a* Clover (*Tritium sativum*), Faba bean (*Vicia faba*), and Wheat (*Triticum aestivum*).

*b* ND: Not detected.

correlation between the contents of studied heavy metals in both soils and plants. The levels of heavy metals in different plants species varied widely, and ranged from 11.7–76.6, 0–3.7, 7.2–38.3, 3.7–18.4, and 9.8–53.2 mg·kg–1 dry matter for Pb, Cd, Ni, Co, and Zn respectively. The highest levels of all studied heavy metals were observed in the plants grown in T&C, while the lowest values were observed in the plants grown in M.C. soil. The levels of heavy metals in the plants grown in the studied soils could be arranged as follows: T&C soil > BD soil > IS soil > T&S soil > M.C. soil.

The normal levels of studied heavy metals in plants are for Pb 5–10, Cd 0.01–0.2, Ni 0.1–5, Co 0.02–1, and Zn 25–150 mg·kg–1 dry matter [30]. While the toxic levels of these elements are 30–300, 5–30, 10–100, 15–50, and 100–400 mg·kg–1 dry matter for Pb, Cd, Ni, Co, and Zn respectively [33,30]. Accordingly, no plant toxicity of studied heavy metals is considered to be possible in M.C. soil, the grown plants in T&S soil had toxic level of Ni, plants grown in T&C and BD soils suffer from Pb, Ni, and Co toxicity, while the growing plants in IS soil suffer from Pb and Ni toxicity. It is worthy to mention that even soils that are polluted with low concentrations of heavy metals can engage in bioaccumulation of heavy metals with time in the higher trophic level's organisms. Therefore, we should not disregard the anthropogenic environmental contamination with traces of heavy metals.

## **4. Conclusions**

Results showed that a clear risk associated with the irrigation of soils and crops with agricultural drainage water mixed with industrial waste effluents in relation with the heavy metal contents. Therefore, the long term of soil irrigated by this water, will cause deterioration to agricultural land, harmful effect on crop quality and quantity, and cause environmental problems. Accordingly, the danger of distribution wastes by such companies containing high concentrations of heavy metals affects the survival in the suffering areas. Therefore, it is important to issue laws and limitations for these companies to prevent them from polluting agricultural soils. Industrial establishments should treat their wastes before disposal and dump them under strict measures. Aqueous wastes, under all circumstances, should not be discharged into irrigation water canals. Factories emitting smokes, gases, and smut must be provided with suitable filters. Newly planned industrial activities should take place away from population masses, as well as from the agricultural land.

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#### **Declaration of interests**

The author declare that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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