Chemical fractionation of some heavy metals in soils irrigated from El-Saff wastewater drainage canal, Egypt

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ABSTRACT
Assessment of heavy metals fractions in soils irrigated with wastewater can directly reflect their bioavailability and contamination level in soil depths. The present study was conducted to assess the heavy metals (Cd, Cu, Pb, Mn, and Fe) fractionation in agricultural soils illegally irrigated with El-Saff wastewater drain, southern Giza Governorate, Egypt. Generally, practices of wastewater irrigation increased pH values in the deeper depths of irrigated soils. Results revealed that long-term wastewater irrigation profusely affected the studied heavy metals fractions in soil depths. Generally, the ranges of studied heavy metals concentrations in soils irrigated with wastewater were apparently different. All fractions were significantly higher in the upper soil depths (0–60 cm and 30–60 cm) than the deeper depths (60–90 cm and 90–120 cm). Heavy metals concentrations varied in the soils as Fe > Mn > Cu > Pb > Cd after irrigation. The heavy metals fractions were dominant in the residual form followed by oxides bound and organically bound fractions. Lower contents of heavy metals in the soil were obtained in the exchangeable fraction. Wastewater irrigation resulted in the transformation of heavy metals into different fractions as residual > oxide associated > organically bound > carbonate associated > exchangeable form. Monitoring of heavy metals concentration in El-Saff wastewater effluent is periodically required.

KEYWORDS
Wastewater, Heavy metals; Soil contamination; Fractionation

Introduction
Wastewater irrigation has been practiced in many arid and semiarid areas due to its fertilization potentials and for the shortage of freshwater. Large amounts of untreated and/or inadequately treated wastewater are currently used by farmers under the uncontrolled condition in many developing countries (Abu-Elela, Farrag, Elbeehairy, & Abou-Hadid, 2021; Farrag, Elbasta, & Ramadan, 2016). Irrigation with wastewater has certain advantages such as providing the essential nutrients and organic matter, saving water and nutrients, and reducing water contamination (Abu-Elela, Farrag, Elbeehairy, & Abou-Hadid, 2021; Zhang & Shen, 2017). Therefore, it is a great temptation for poor farmers to irrigate crops with wastewater as it can reduce the crop production cost by 10%–20% (Scott et al., 2010). On the other hand, many environmental, sanitary, and health risks are also associated with the use of wastewater for crop irrigation due to the presence of toxic contaminants and microbes (Abu-Elela, Farrag, Elbeehairy, & Abou-Hadid, 2021). Irrigation with untreated and/or inadequately treated wastewater can lead to heavy metals accumulation in agricultural soils and ultimately enter the food chain via agricultural crops (Nawaz, Khurshid, & Ranjha, 2006). Although the total heavy metal content in soil is useful for characterizing the distribution of contaminants, the bioavailability and behavior of heavy metals in soils do not always coincide with the total content (Han, 2007). In solution, heavy metals can be found in free form or complex. In the formation of a complex or a unit, for example, an ion, as a central group, can attract and form an intimate association with other atoms or molecules. Therefore, the chemical forms and speciation of heavy metals when assessing their actual dynamics in the environment, soil, in particular, need to be known (Jalali & Khaniari, 2008). The same authors reported that incubation using heavy metal-spiked soils resulted in transforming heavy metal pools into more stable fractions over time (Jalali & Khaniari, 2008). The slow process of transformation of heavy metal pools is largely controlled by both the redistribution of heavy metals among various solid-phase components and the slow distribution of surface-sorbed or surface-precipitated heavy metal into particles (Han, 2007). These complexes can occur between a metal and an inorganic binder, such as anions, where the electron-sharing atom is oxygen and has a preference for hard metals. However, a complex between the metal and an organic ligand can also be formed, which can be classified as hard (usually the carboxylic and phenolic sites) and soft organic matter sites, which are the sites...
that have S and N (Ferreira, Brunetto, Giachini, & Soares, 2014). Liang, Yang, Xu, Wang, & Chen (2012) reported that the solid phase components, such as clay minerals and manganese and iron oxides, would control the actual dynamics of heavy metals in polluted soil under wastewater irrigation regimes.

Heavy metals behavior in Egyptian soil regarding the wastewater irrigation practices needs more studies for the enhancement of soil quality and human health protection. Therefore, the current study aimed at characterizing the heavy metals (Cd, Cu, Pb, Mn, and Fe) in soils of agricultural lands in the El-Saff area after long-term unlawful irrigation with El-Saff wastewater drain southern Giza governorate, Egypt. Previous studies on wastewater-irrigated soil in the study area focused on the total metals content (Farrag et al., 2016) without any point on species and bioavailability of these metals, which can reduce their effects on the environment.

Materials and methods

Description of the study area

The El-Saff area (29°30–29°45 N; 31°15–31°25 E) is situated at the southern part of Helwan municipality, Giza Governorate, on the east bank of the Nile River and western of El-Saff wastewater drain. The study was conducted at the El-Saff area, and some GPS locations are shown in Table 1 during two growing seasons of 2017 where it has been noticed that the farmers illegally use the drain to irrigate different cultivated crops in this area. Water samples and soil samples at depths of 0–30, 30–60, 60–90, and 90–120 cm were taken from six sites along El-Saff drain and its surrounding agricultural fields to assess the anticipated pollution risk hazards due to their irresponsible behavior.

Water and soil samples

Water samples were collected from each site in pre-cleaned high-density polyethylene bottles, which were prepared according to the method described by Environment Protection Authority, (EPA Guidelines, 2007) and Rocky Mountain Research Station (RMRS, 2012). Samples were brought into the laboratory in an ice tank and stored at 4°C until analysis on the next day. As for soil samples, they were air-dried, sieved through a < 0.2 mm sieve, and stored in the labeled polythene sampling bags.

Analytical methods

Electrical conductivity (EC) in water and soil paste extract was determined using an EC meter (model WTW Series Cond 720); pH values in water and soil suspensions (1:2.5) were determined by using a pH meter (model WTW Series pH 720); soluble cations and anions were determined in water and soil according to the methods proposed by ICARDA International Center for Agricultural Research in the Dry Areas (2013). The following determinations were made based on the methods described in AOAC (1995): Soluble compounds (P, Fe, Mn, Cu, Cd, Cr, Ni, and Pb) in water were acidified with HNO₃ (1 mL of acid for 100 mL of water), as stated by Eaton, Clesceri, Rice, and Greenberg (2005). Available compounds (Fe, Mn, Cu, Cd, and Pb) in soil were extracted according to the method of Soltanpour and Schwab (1991). Total elements (Fe, Mn, Cu, Cd, and Pb) were digested by using aqua regia (HCl and HNO₃) according to Cottenie, Varloo, Kiekens, Velghe, and Camerlynck (1982) and ICARDA International Center for Agricultural Research in the Dry Areas (2013). Elements in water and soil were determined for P, Fe, Mn, Cu, Cd, Cr, Ni, and Pb using inductively coupled plasma (ICP) Spectrometry (model Ultima 2 JY Plasma) according to Environmental Protection Agency (EPA, 1991).

Sequential extraction procedures were used to determine the metal fractionation in the soils (Tessier, Campell, & Bisson, 1979). The method consists of the following steps: the exchangeable bond fraction was extracted with magnesium chloride, the carbonate bond fraction was extracted with sodium acetate, the Fe-Mn oxide bond fraction was extracted with hydroxylamine hydrochloride/acetic acid, the organically bound fraction was extracted with nitric acid/hydrogen peroxide/ammonium acetate, and the residual fraction was extracted with hydrochloric/perchloric acids.

Results and discussion

Characteristics of wastewater

Table 2 represents the quality of wastewater of El-Saff wastewater drain used for growing vegetables in the studied area. The pH values were moderately alkaline and within the national and FAO limits (6.5–8.5) for irrigation use. The EC values ranged from 0.75 to 1.09 with a mean value of 0.89 (dSm⁻¹), indicating that analyzed wastewater samples are within the allowable EC range (slight to moderate restriction) as stated by FAO guidelines (0.7–3.0 m⁻¹) for irrigation water. The

| Sites          | GPS          |
|----------------|--------------|
| Arab Abu Said  | 29°42′ 21.1″N 31°23′ 12.1″E |
| El-Shorafa     | 29°44′ 29.8″N 31°21′ 47.9″E |
| El-Akhsas      | 29°42′ 05.1″N 31°22′ 59.0″E |
| Ghammaza Al Qobra | 29°43′ 32.8″N 31°22′ 22.3″E |
| Ghammaza Al Soghra | 29°43′ 04.9″N 31°22′ 41.9″E |
| Arab Al Hesar  | 29°43′ 03.8″N 31°22′ 42.1″E |
The OM of the wastewater-irrigated soils ranged from 1.04% to 4.29% in the surface layers (0–30 cm), whereas its values ranged from 0.84% to 1.22% in the deeper layers (90–120 cm). This could be explained that long-term irrigation with wastewater profoundly affected the soil chemical and physical composition through the soil layers. Similar findings were reported by Farrag et al. (2016) in wastewater-irrigated soils along El-Saff wastewater drain. However, using wastewater in irrigation could enrich soils with OM (Abdel-Ewiseh, 2018). Organic matter is the primary contributor to retain heavy metals in the soil through the formation of complexes or exchangeable forms (Salman, Abu El Ella, & Elnazer, 2018).

The bioavailability and toxicity of metals decrease with the increasing particle size (Gerdelidani et al., 2021). The texture of the soil layers remained unchanged after wastewater irrigation in both El-Shorafa, Ghammaza Al Qobra, and Ghammaza Al Sohra locations, and also, the results exhibited that wastewater irrigation slightly increased the percent of clay and loam at soil depths of 30–60 cm and 60–90 cm in Arab Al Hesar and El-Akhas and the surface layer of Arab Abu Said locations. Loamy sand class of soil texture was recorded in soil samples collected from agricultural fields irrigated with El-Saff wastewater drain (Farrag et al., 2016) in the studied area. The content of heavy metals in soil is inversely proportional to the soil particle sizes and accumulates in the clay and silt fractions of soil (Salman et al., 2018).

The results in Table 3 revealed that wastewater irrigation decreased the pH values of upper soil depths. The pH of the wastewater-irrigated soils ranged from 6.11 to 8.65 and 6.2 to 7.66 in both 0–30 cm  

### Characteristics of wastewater-irrigated soils

Soil sampled from agricultural fields irrigated with El-Saff wastewater drain showed higher values of pH, electrical conductivity (EC), calcium carbonate (CaCO₃), and bulk density (BD) in the upper depths (0–30 cm and 30–60 cm) as compared to the deeper depths (60–90 cm and 90–120 cm) Table 3. The results revealed that wastewater irrigation increased the organic matter (OM) values of the upper soil depths.
| Locations          | Soil depth (cm) | Soil particles size distribution (%) | Texture pH | EC | CaCO$_3$ | OM | Bd |
|--------------------|----------------|-------------------------------------|------------|----|----------|----|----|
|                    |                | Coarse Sand | Fine Sand | Silt | Clay | 1:2.5 | ds m$^{-1}$ | % | g cm$^{-3}$ |
| Arab Al Hesar area | 0-30           | 92.46       | 5.43      | 0.46 | 2.07 | S     | 8.65 | 0.25 | 3.00 | 2.79 | 1.24 |
|                    | 30-60          | 51.89       | 10.90     | 19.00 | 6.21 | S     | 6.56 | 0.36 | 2.21 | 2.71 | 1.28 |
|                    | 60-90          | 54.65       | 12.14     | 16.41 | 6.80 | S     | 6.56 | 0.15 | 3.00 | 2.16 | 1.29 |
|                    | 90-120         | 78.74       | 0.21      | 15.73 | 5.32 | S     | 7.43 | 0.31 | 3.53 | 1.22 | 1.56 |
| El-Akhas area      | 0-30           | 70.92       | 6.83      | 15.68 | 6.57 | S     | 6.11 | 0.39 | 1.57 | 4.15 | 1.22 |
|                    | 30-60          | 36.60       | 18.21     | 21.40 | 6.57 | S     | 6.20 | 0.32 | 1.60 | 4.29 | 1.25 |
|                    | 60-90          | 43.70       | 14.10     | 22.02 | 0.00 | S     | 6.78 | 0.45 | 2.00 | 3.24 | 1.28 |
|                    | 90-120         | 64.58       | 15.34     | 21.41 | 3.23 | S     | 6.78 | 0.33 | 3.01 | 1.11 | 1.50 |
| El-Shorafa area    | 0-30           | 63.97       | 27.41     | 1.12  | 7.44 | S     | 6.95 | 0.39 | 2.16 | 1.35 | 1.24 |
|                    | 30-60          | 65.01       | 25.78     | 1.50  | 8.17 | S     | 7.05 | 0.34 | 2.00 | 1.09 | 1.28 |
|                    | 60-90          | 66.17       | 25.20     | 2.00  | 7.51 | S     | 7.25 | 0.28 | 1.90 | 1.32 | 1.29 |
|                    | 90-120         | 75.20       | 23.42     | 1.22  | 6.76 | S     | 7.48 | 0.30 | 1.76 | 1.01 | 1.45 |
| Ghammaza Al Qobra area | 0-30      | 60.25       | 60.25     | 1.28  | 17.73 | S     | 6.90 | 0.30 | 1.90 | 2.79 | 1.22 |
|                    | 30-60          | 61.15       | 21.13     | 2.37  | 15.35 | S     | 6.95 | 0.28 | 1.60 | 2.67 | 1.25 |
|                    | 60-90          | 58.10       | 24.30     | 2.22  | 16.35 | S     | 7.13 | 0.24 | 1.58 | 2.04 | 1.28 |
|                    | 90-120         | 66.37       | 22.31     | 1.32  | 6.76 | S     | 7.87 | 0.30 | 1.45 | 1.00 | 1.43 |
| Arab Abu Said      | 0-30           | 77.45       | 15.56     | 1.66  | 4.82 | S     | 7.46 | 1.25 | 2.60 | 1.19 | 1.39 |
|                    | 30-60          | 81.75       | 16.88     | 3.51  | 7.83 | S     | 7.65 | 1.71 | 2.30 | 1.03 | 1.34 |
|                    | 60-90          | 73.07       | 16.32     | 3.04  | 7.54 | S     | 7.64 | 1.89 | 2.51 | 1.00 | 1.40 |
|                    | 90-120         | 77.83       | 16.87     | 2.36  | 5.33 | S     | 7.45 | 1.78 | 2.00 | 0.84 | 1.66 |
| Ghammaza Al Soghra | 0-30           | 60.82       | 28.24     | 2.65  | 8.39 | S     | 7.40 | 3.39 | 2.05 | 1.32 | 1.38 |
|                    | 30-60          | 56.54       | 30.32     | 4.66  | 8.48 | S     | 7.66 | 3.60 | 2.10 | 1.22 | 1.37 |
|                    | 60-90          | 55.12       | 27.97     | 7.79  | 9.12 | S     | 7.56 | 4.65 | 1.98 | 1.10 | 1.43 |
|                    | 90-120         | 77.98       | 25.33     | 5.34  | 4.12 | S     | 7.88 | 4.33 | 1.53 | 0.92 | 1.69 |

S: Sandy; SCL: Sandy Clay Loam; SC: Sandy Clay; EC: Electrical Conductivity; CaCO$_3$: Calcium Carbonate; OM: Organic Matter; Bd: Bulk Density
and 30–60 cm, respectively, whereas its values ranged from 6.56 to 7.64 and 6.78 to 7.88 in both 60–90 cm and 90–120 cm, respectively. These slight increases in soil pH of the upper depths as a function of the wastewater irrigation may be attributed to the alkalization effect of contained cations such as Mg, Ca, and Na in the water (Alghobar, Ramachandra, & Suresha, 2014). However, the alkaline nature of most studied soils can enhance the precipitation of heavy metals because their solubility is inversely proportional to the pH of the soil. The alkaline environment will lead to the accumulation of heavy metals (Salman et al., 2021).

The average values of EC in soil are shown in Table 3; they recorded 1.08 and 1.10 dS m⁻¹ in the upper depths, 0–30 cm and 30–60 cm, respectively, whereas the average value of EC recorded 1.55 and 1.47 dS m⁻¹ in the deeper depths, 30–60 cm and 60–90 cm, respectively. Elevated EC values indicated that the use of industrial WW for irrigation can lead to an accumulation of salts in the soils. The lower EC values of upper depths are due to salt leaching by percolated waters after intensive furrow irrigation practiced by farmers in the study area (Farrag et al., 2016).

The concentrations of studied heavy metals in soils as shown in Table 3 were in the sequence of Fe > Mn > Cu > Pb > Cd for both upper and deeper depths and were higher than their concentration in wastewater of El-Saff drain. Except for Cd (4.71 mg kg⁻¹), all the mean concentrations of the studied metals in soil irrigated with wastewater (52.74 for Cu, 42.92 for Pb, 202.079 for Fe, and 63.58 for Mn, mg kg⁻¹) were within the FAO/WHO (2007) limits (3 for Cd, 140 for Cu, 300 for Pb, and 400 for Mn, mg kg⁻¹). The alkaline environment of study soils (mean pH >7) is the most important factor indicating the low mobility of studied metals. pH is the key parameter influencing the mobility of heavy metals (McBride, 1994).

The results showed that heavy metals fractions were significantly higher in the upper depths as compared to the deeper depths in all studied locations. Generally, heavy metals predominantly appeared in the residual form followed by oxide-associated form and organically bound form. According to Han (2007), the residual fraction is the most stable fraction in soils and it is affected by the parent material, soil properties, and climate condition. However, heavy metal fractions differed in the order of residual metal > oxide associated metal > organically bound metal > carbonate associated metal > exchangeable metal. The same author reported that soil OM has a higher affinity for heavy metals adsorption, which can explain the medium increase in soil heavy metals in organic fraction (Han, 2007).

The ranges of Cd concentrations in soils irrigated with El-Saff wastewater drain are presented in Table 4. Among the sampling fields subjected to wastewater
Table 5. Soil total and DTPA-extractable and fractions distribution of Cu at different sites of the El-Saff area.

| Locations         | Soil Depth (cm) | Concentration (mg kg\(^{-1}\)) | Fractions content (mg kg\(^{-1}\)) |
|-------------------|-----------------|---------------------------------|-----------------------------------|
|                   |                 | Total DTPA Ex. Carb. Ox. Org Res. |
| Arab Abu Said     | 0–30            | 12.52 n.d. 1.04 0.56 8.44 2.07 35.08 |
|                   | 30–60           | 44.16 0.25 0.71 0.21 3.43 1.21 11.09 |
|                   | 60–90           | 54.3 0.33 0.44 0.29 4.21 1.00 11.41 |
|                   | 90–120          | 64.82 0.45 0.54 0.25 3.31 1.15 11.62 |
| El-Shorafa        | 0–30            | 22.54 n.d. 2.06 0.50 15.46 71.07 62.29 |
|                   | 30–60           | 42.50 1.54 1.23 0.22 5.46 24.85 18.35 |
|                   | 60–90           | 64.94 1.79 0.56 0.22 5.06 15.97 13.28 |
|                   | 90–120          | 71.23 1.85 0.58 0.12 3.47 11.35 12.22 |
| Ghammaza Al Qobra | 0–30            | 17.51 n.d. 4.91 5.01 12.9 27.90 12.92 |
|                   | 30–60           | 80.12 3.82 3.21 4.92 10.51 20.31 10.10 |
|                   | 60–90           | 86.12 4.55 2.20 3.54 4.21 14.00 7.82 |
|                   | 90–120          | 90.23 5.01 1.92 2.51 7.20 11.72 6.51 |
| Ghammaza Al Soghra| 0–30            | 21.45 n.d. 5.95 6.22 17.5 30.21 21.21 |
|                   | 30–60           | 38.24 1.54 5.00 5.90 16.51 20.91 12.21 |
|                   | 60–90           | 50.75 1.66 4.22 3.72 12.41 12.51 11.75 |
|                   | 90–120          | 66.37 1.65 3.71 2.21 10.72 10.29 9.91 |
| Arab Al Hesar     | 0–30            | 22.98 n.d. 4.35 28.24 40.58 15.09 45.65 |
|                   | 30–60           | 54.64 0.27 1.69 11.04 17.54 5.23 20.90 |
|                   | 60–90           | 62.45 0.45 1.36 7.23 10.67 3.39 14.08 |
|                   | 90–120          | 71.56 0.55 0.69 3.21 4.94 1.41 7.10 |
| El-Akhsas         | 0–30            | 14.98 n.d. 7.27 27.22 46.27 14.31 44.17 |
|                   | 30–60           | 54.39 2.65 1.84 7.28 13.64 4.37 15.31 |
|                   | 60–90           | 67.58 3.78 1.01 4.22 7.08 2.27 8.58 |
|                   | 90–120          | 89.47 4.22 1.31 3.86 6.51 1.99 8.05 |

Ex.: Exchangeable-bound; Carb.: Carbonate-bound; Ox.: Oxide-bound; Org: Organically bound; Res: Residual fraction

Table 6. Soil total and DTPA-extractable and fractions distribution of Pb at different sites of the El-Saff area.

| Locations         | Soil Depth (cm) | Concentration (mg kg\(^{-1}\)) | Fractions content (mg kg\(^{-1}\)) |
|-------------------|-----------------|---------------------------------|-----------------------------------|
|                   |                 | Total DTPA Ex. Carb. Ox. Org Res. |
| Arab Abu Said     | 0–30            | 17.61 n.d. 0.84 1.75 2.12 21.85 15.36 |
|                   | 30–60           | 49.03 0.90 0.26 0.52 0.68 6.46 4.92 |
|                   | 60–90           | 55.14 1.26 0.29 0.56 0.71 4.99 3.39 |
|                   | 90–120          | 59.27 1.32 0.12 0.26 0.37 1.04 1.05 |
| El-Shorafa        | 0–30            | 4.12 n.d. 2.62 4.93 5.11 54.19 36.41 |
|                   | 30–60           | 19.55 0.36 1.03 1.75 2.46 18.21 12.63 |
|                   | 60–90           | 39.97 0.71 0.68 1.23 1.56 11.07 7.52 |
|                   | 90–120          | 40.16 0.84 0.51 0.83 1.19 5.78 4.05 |
| Ghammaza Al Qobra | 0–30            | 13.90 n.d. 0.56 0.41 7.91 2.17 0.12 |
|                   | 30–60           | 31.95 1.16 0.86 0.67 3.44 1.40 0.10 |
|                   | 60–90           | 84.47 1.72 0.23 0.57 2.72 1.21 0.04 |
|                   | 90–120          | 92.21 1.85 0.17 0.49 2.05 1.10 0.07 |
| Ghammaza Al Soghra| 0–30            | 15.30 n.d. 0.17 0.76 1.71 8.32 3.21 |
|                   | 30–60           | 51.24 0.67 0.12 0.62 0.90 5.44 2.51 |
|                   | 60–90           | 64.27 1.32 0.10 0.51 0.82 3.47 1.92 |
|                   | 90–120          | 70.33 1.45 0.09 0.40 0.40 2.83 1.31 |
| Arab Al Hesar     | 0–30            | 10.82 n.d. 2.92 11.29 13.78 6.31 21.56 |
|                   | 30–60           | 22.54 1.32 0.57 2.39 3.56 1.55 5.78 |
|                   | 60–90           | 63.27 1.65 0.41 2.14 2.95 1.18 4.56 |
|                   | 90–120          | 84.26 1.91 0.28 1.75 2.05 0.89 3.24 |
| El-Akhsas         | 0–30            | 5.23 n.d. 1.29 14.23 20.71 8.43 12.79 |
|                   | 30–60           | 20.12 0.42 0.62 3.23 5.16 1.87 8.81 |
|                   | 60–90           | 54.32 0.65 0.39 2.33 3.41 1.24 5.41 |
|                   | 90–120          | 61.11 1.25 0.29 1.63 2.09 0.73 3.67 |

Ex.: Exchangeable-bound; Carb.: Carbonate-bound; Ox.: Oxide-bound; Org: Organically bound; Res: Residual fraction
irrigation, the average concentration of residual Cd was 1.52 mg kg$^{-1}$, organically bound Cd was 1.34 mg kg$^{-1}$, oxide bound Cd was 1.13 mg kg$^{-1}$, carbonate-associated Cd was 0.69 mg kg$^{-1}$, and the exchangeable form of Cd was 0.22 mg kg$^{-1}$. Among the wastewater-irrigated fields, the average concentration of residual Cd organically bound Cd and oxide-bound Cd was 1.90, 1.79, and 1.52 mg kg$^{-1}$, respectively, in the upper depths and 1.14, 0.90, and 0.73 mg kg$^{-1}$, respectively in the deeper depths. The other fraction forms of Cd, namely, carbonate and exchangeable forms, were found in smaller quantities. Usman and Ghallab (2006) reported that irrigation of soil with wastewater resulted in the transformation of metals from the carbonate fraction toward the exchangeable, Fe–Mn oxide, and organic fraction for Zn, toward the exchangeable, organic, and residual fraction for Cu, and toward the exchangeable fraction for Cd.

Copper concentrations were substantially high in wastewater-irrigated fields. The Cu fractions differed among sampling locations after long-term wastewater irrigation (Table 5). The Cu fractions differed in the order: residual Cu (2.51–62.29 mg kg$^{-1}$) > oxide bound Cu (3.31–46.27 mg kg$^{-1}$) > carbonate bound Cu (0.12–28.24 mg kg$^{-1}$) > organically bound Cu (1–71.07 mg kg$^{-1}$) > exchangeable Cu (0.44–7.27 mg kg$^{-1}$). The contents of Cu in deeper soil depths were observed in smaller quantities, regardless of the type of Cu fraction. The majority of Cu contents in the soils and sediments were associated with the residual fraction (Hickey & Kittrick, 1984; Ma & Rao, 1997). Kabala, Karczewska, Szopka, and Wilk (2011) reported that the largest fraction of Cu and Pb in wastewater-irrigated soils was strongly bound in a residual form, while exchangeable and the other labile fractions were negligible.

The extractability of Pb in collected soil samples varied considerably depending on soil depths for each location (Table 6). Lead was found to be dominant in the organically bound Pb, which ranged from 1.4 to 54.19 mg kg$^{-1}$ in the upper depths, whereas Pb concentrations varied from 0.73 to 11.7 mg kg$^{-1}$ in the deeper depths (Table 6). Astrid & Fernando (1996) reported that the amount of Pb extracted with the cleaning solution was found to be related to the fractions associated with oxides and organic matter (and/or sulfides). Lead in the residual form ranged from 0.10 to 36.41 mg kg$^{-1}$ in the upper depths. In the deeper depths, the residual form of Pb ranged from 0.40 to 7.52 mg kg$^{-1}$. Oxide-associated Pb was higher in El-Akhsas (20.71 mg kg$^{-1}$) and lowest in Arab Abu Said (0.37 mg kg$^{-1}$) studied areas. The deeper depths recorded a significantly lower concentration of oxide-associated Pb. Exchangeable Pb ranged from 0.12 to 2.92 mg kg$^{-1}$ in the upper depths of sampling sites irrigated with wastewater. According to Astrid & Fernando, (1996), Pb was predominantly

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**Table 7.** Soil total and DTPA-extractable and fractions distribution of Fe at different sites of the El-Saff area.

| Locations         | Soil Depth (cm) | Concentration (mg kg$^{-1}$) | Frations content (mg kg$^{-1}$) |
|-------------------|-----------------|------------------------------|---------------------------------|
|                   |                 | Total                        | DTPA                            |
|                   |                 | Ex.                          | Carb.                           |
|                   |                 | Ox.                          | Org.                            |
|                   |                 | Res.                         |                                 |
| Arab Abu Said     | 0–30            | 33.52                        | n.d                             |
|                   | 30–60           | 252.42                       | 8.30                            |
|                   | 60–90           | 617.44                       | 19.23                           |
|                   | 90–120          | 654.27                       | 20.14                           |
| El-Shorafa        | 0–30            | 21.12                        | n.d                             |
|                   | 30–60           | 127.81                       | 4.16                            |
|                   | 60–90           | 210.52                       | 9.25                            |
|                   | 90–120          | 258.25                       | 10.31                           |
| Ghammaza Al Qobha | 0–30            | 100.81                       | n.d                             |
|                   | 30–60           | 205.20                       | 11.65                           |
|                   | 60–90           | 372.78                       | 18.96                           |
|                   | 90–120          | 432.52                       | 20.56                           |
| Ghammaza Al Soghra| 0–30            | 21.35                        | n.d                             |
|                   | 30–60           | 59.68                        | 5.69                            |
|                   | 60–90           | 88.34                        | 10.68                           |
|                   | 90–120          | 100.14                       | 19.67                           |
| Arab Al Hesar     | 0–30            | 54.45                        | n.d                             |
|                   | 30–60           | 158.78                       | 8.30                            |
|                   | 60–90           | 196.37                       | 19.58                           |
|                   | 90–120          | 201.21                       | 22.47                           |
| El-Akhsas         | 0–30            | 95.39                        | n.d                             |
|                   | 30–60           | 123.54                       | 11.65                           |
|                   | 60–90           | 210.35                       | 18.96                           |
|                   | 90–120          | 253.47                       | 20.56                           |

Ex.: Exchangeable-bound; Carb.: Carbonate-bound; Ox.: Oxide-bound; Org: Organically bound; Res: Residual fraction.
accumulated in the residual fraction and in the fraction associated with Fe/Mn oxides. In the deeper depths, the concentration of exchangeable Pb varied from 0.10 to 0.68 mg kg$^{-1}$. Carbonate-associated Pb ranged from 0.41 to 14.23 mg kg$^{-1}$ in the upper depths. The Pb concentrations associated with carbonate were found to be between 0.51 and 3.23 mg kg$^{-1}$ in the deeper depths. In the less-contaminated fine-textured soil, Pb was distributed in the following order: residual > Fe-Mn oxides occluded > organically complexed > exchangeable and specifically adsorbed, while the order for sandy soils was residual > organically complexed > Fe-Mn oxides occluded > exchangeable and specifically adsorbed (Kahala & Singh, 2001).

The Fe concentrations were found to be higher in the soil’s deeper depths as compared to the upper depths in Table 7. In all studied soil locations, the Fe fractions differed as residual > oxide bound > organically bound > carbonate associated > exchangeable. Bushra et al. (2019) found that Fe fractions were dominant in the residual form followed by oxide-bound and carbonate-associated fractions in wastewater-irrigated soils and lower contents of Fe in the soil were obtained in the exchangeable fraction. The average concentration of residual Fe was 72.36 mg kg$^{-1}$, oxide-bound Fe was 39.55 mg kg$^{-1}$, organically bound Fe was 31.03 mg kg$^{-1}$, carbonate-associated Fe was 25.09 mg kg$^{-1}$, and exchangeable Fe was 5.69 mg kg$^{-1}$. Among the wastewater-irrigated fields, the residual form of Fe was highest in both fields of El-Shorafa (280.6 mg kg$^{-1}$) and El-Akhsas (279.9 mg kg$^{-1}$) and lowest in Ghammaza Al Qobra (10.71 mg kg$^{-1}$). Residual Fe ranged from 20 to 280.6 mg kg$^{-1}$ in the upper depths and from 10.71 to 77.11 in the deeper depths. Oxide-bound Fe ranged from 8.65 to 258.9 mg kg$^{-1}$ in the upper depths and from 3.24 to 37.99 mg kg$^{-1}$ in the deeper depths. Organically bound Fe ranged from 5.92 to 180.6 mg kg$^{-1}$ in the upper depths and from 4.21 to 60.38 mg kg$^{-1}$ in the deeper depths, whereas carbonate-bound Fe and exchangeable Fe ranged from 3.23 to 157.4 mg kg$^{-1}$ and from 0.71 to 36.4 mg kg$^{-1}$ in all studied wastewater-irrigated fields, respectively.

In soils sampled from the fields irrigated with El-Saff wastewater drain, the average concentrations of residual Mn were 2.93 mg kg$^{-1}$, oxide-bound Mn was 0.74 mg kg$^{-1}$, carbonate-associated Mn was 1.11 mg kg$^{-1}$, organically bound Mn was 1.51 mg kg$^{-1}$, and the exchangeable form of Mn was 2.58 mg kg$^{-1}$ as shown in Table 8. Among the wastewater-irrigated fields, the exchangeable form of Mn was the highest in the upper depth (0–30 cm) of wastewater-irrigated fields of El-Akhsas (7.21 mg kg$^{-1}$), whereas oxide-bound Mn recorded the lowest value (0.11 mg kg$^{-1}$) in the deeper depth (90–120 cm) of the Arab Al Hesar sampling area. Similar

### Table 8. Soil total and DTPA-extractable fractions distribution of Mn at different sites of El-Saff area

| Locations       | Soil Depth (cm) | Concentration (mg kg$^{-1}$) | Frac. content (mg kg$^{-1}$) |
|-----------------|-----------------|------------------------------|-----------------------------|
|                 |                 | Total | DTPA | Ex. | Carb. | Ox. | Org | Res. |
| Arab Abu Said   | 0-30            | 22.44 | n.d. | 3.11 | 1.21 | 0.60 | 1.92 | 2.51 |
|                 | 30-60           | 26.75 | 1.52 | 3.00 | 1.10 | 0.47 | 1.32 | 2.00 |
|                 | 60-90           | 58.98 | 1.96 | 2.12 | 0.41 | 0.31 | 1.20 | 1.75 |
|                 | 90-120          | 78.27 | 2.45 | 2.00 | 0.32 | 0.13 | 1.00 | 1.22 |
| El-Shorafa      | 0-30            | 33.71 | n.d. | 5.92 | 1.92 | 0.91 | 1.21 | 3.39 |
|                 | 30-60           | 56.99 | 3.62 | 4.52 | 1.13 | 0.80 | 1.01 | 2.11 |
|                 | 60-90           | 89.47 | 4.17 | 4.01 | 1.00 | 0.84 | 0.85 | 2.00 |
|                 | 90-120          | 100.26| 5.94 | 3.11 | 0.90 | 0.13 | 0.52 | 1.52 |
| Ghammaza Al Qobra| 0-30         | 54.04 | n.d. | 2.91 | 1.22 | 0.81 | 1.92 | 2.11 |
|                 | 30-60           | 56.47 | 4.43 | 1.78 | 1.00 | 0.75 | 1.72 | 2.00 |
|                 | 60-90           | 99.36 | 5.37 | 1.11 | 0.92 | 0.81 | 1.00 | 1.72 |
|                 | 90-120          | 110.38| 6.04 | 0.95 | 0.81 | 0.27 | 0.95 | 1.00 |
| Ghammaza Al Soghra| 0-30        | 44.35 | n.d. | 6.72 | 2.00 | 1.22 | 1.75 | 4.21 |
|                 | 30-60           | 64.87 | 5.32 | 5.10 | 1.59 | 1.00 | 1.22 | 3.11 |
|                 | 60-90           | 87.96 | 6.44 | 4.99 | 1.30 | 0.95 | 0.99 | 2.95 |
|                 | 90-120          | 99.67 | 6.97 | 3.21 | 1.00 | 0.93 | 0.75 | 2.13 |
| Arab Al Hesar   | 0-30            | 20.45 | n.d. | 6.59 | 1.23 | 0.82 | 2.23 | 5.41 |
|                 | 30-60           | 44.37 | 1.75 | 5.71 | 1.11 | 0.75 | 2.12 | 4.52 |
|                 | 60-90           | 56.43 | 2.03 | 2.11 | 1.00 | 0.61 | 2.01 | 3.11 |
|                 | 90-120          | 71.65 | 2.88 | 1.72 | 0.82 | 0.11 | 1.13 | 2.21 |
| El-Akhsas       | 0-30            | 43.25 | n.d. | 7.21 | 1.70 | 1.52 | 3.01 | 6.00 |
|                 | 30-60           | 50.57 | 2.52 | 6.66 | 1.21 | 1.03 | 2.51 | 5.19 |
|                 | 60-90           | 66.79 | 5.15 | 5.71 | 1.00 | 0.89 | 1.97 | 4.99 |
|                 | 90-120          | 88.45 | 6.78 | 4.11 | 0.80 | 1.00 | 2.00 | 3.12 |

Ex.: Exchangeable-bound; Carb.: Carbonate-bound; Ox.: Oxides-bound; Org.: Organic-bound; Res.: Residual fraction
results have been observed by Yasser (2008) who listed the associated Mn in soils irrigated with contaminated water in the decreasing order of Residual > Fe-Mn oxides > Organic > Carbonate > Exchangeable > Water Soluble.

Conclusion

This study assessed some heavy metals (Cd, Cu, Pb, Mn, and Fe) fractions in agricultural soils irrigated for a long term with wastewater. Results revealed that long-term wastewater irrigation substantially affected the studied heavy metals fractions in soil depths. All fractions were significantly higher in the upper soil depths (0–30 cm and 30–60 cm) than the deeper (60–90 cm and 90–120 cm) depths. The heavy metals fractions were dominant in the residual form followed by oxide-bound and organically bound fractions. Lower contents of heavy metals in the soil were obtained in the exchangeable fraction. Wastewater irrigation soils showed heavy metals fractions in residual > oxide-associated > organically bound > carbonate-associated > exchangeable forms in the study area. Fractionation of heavy metals is periodically required to assess their binding form, toxicity, and availability in the agricultural soils of the study area.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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