# Remobilization of selected metal ions from Nile sediment (Egypt) according to sequential extraction and metal-EDTA complex

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# Remobilization of selected metal ions from Nile sediment (Egypt) according to sequential extraction and metal–EDTA complex

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River sediments are basic components of our environment, providing nutrients for living organisms and serving as sinks for deleterious chemical species. The metal contents may be remobilized and released back into waters with changes in environmental conditions, thus affecting living organisms and human activities. This paper aims to determine the effect of a synthetic anthropogenic chelating agent (EDTA) as industrial discharges on the remobilization of several metals (Cu, Zn, Cd, and Pb) in River Nile sediments (at Aswan and Mansoura cities) under different concentrations and pH values, and to investigate the influence of metal–EDTA complexes on this remobilization. For these purposes, sequential extraction and experiments on the effect of pH and metal EDTA complex were carried out on the two representative sediment samples south and north of the River Nile in Egypt. The results of sequential extraction show that most of metal contents present in the residual form (Cu, 11.36–72.34%; Pb, 29.64–66.67%; and Zn, 43.76–50.09% at Aswan and Mansoura, respectively). Non-residual fractions which may be available for the remobilization by EDTA represented anthropogenic (industrial, agriculture, and domestic discharges) and lithiopogenic (metals bound to Fe and Mn oxides) sources. A clear increase was detected for Cu and Zn remobilization from the increase in EDTA concentrations, in contrast, Cd independent of the EDTA concentration and slight influence on Pb content. The remobilization of metals as a function of pH exhibited. The metals were greatly remobilized under the complexing action of EDTA, showing that some of these elements were adsorbed on the sediments. The remobilization rate of metals was dependent upon the added metal–EDTA complex (with the exchange rate being in the order Ca–EDTA > Zn–EDTA > Cd–EDTA > Cu–EDTA > Pb–EDTA), due to the stability constant of the metal–EDTA complex. The results of these experiments showed that heavy metals are greatly remobilized under the complexing action of EDTA when it is present in excess, so all precautions should be taken to prevent any wastewater containing EDTA or any chelating agents discharging directly or indirectly via the River Nile stream because most EDTA remains in the aquatic phase. The ability of this portion to remobilize metals from sediments should be taken into account.

*Keywords*: Nile sediments; Metal ions; Remobilization; Sequential extraction; Metal–EDTA complex

## 1. Introduction

Sediments are usually considered a sink for trace metals, but they can also become a source under certain conditions. Trace metals are then able to move towards the water column or

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accumulate in plants and, consequently, contaminate the food chain [1]. In recent years, studies on the possible health and ecological effects of accumulated toxic metals in sediments have been published. Measurements of availability and mobility are required in order to understand the behaviour of heavy metals in such samples and to prevent potential toxic hazards. Metals in river sediments can be bound to various compartments: adsorbed on clay surfaces or iron and manganese oxyhydroxides; present in lattice of secondary minerals like carbonates, sulphates, or oxides; occluded in amorphous materials such as iron and manganese oxyhydroxides; and complexed with organic matter or lattice of primary materials such as silicate. Trace-metal speciation studies are important because slight changes in metal availability and in environmental conditions can make these elements toxic to animals and plants [2]. In order to study metal speciation in sediments, leaching/extraction tests are widely used for the assessment of heavy-metal mobilization [3, 4]. Alternatively, sequential extraction procedures, which define the metal activity by the analytical schemes, are preferred [5]. In recent years, both remobility and chemical availability of heavy metal affected by redox and pH conditions have been noted [6–11], indicating that acidic and chelating agents are most effective in removing heavy metals from sediment. From the point of remediation, the remobilization of heavy metals from sediment using chemical techniques (acidic and chelating agents) is needed especially for the disposal of dredged sediment [7]. Metal ions are strongly bound to iron and manganese oxides at neutral pH. Several processes are capable of releasing metal ions back into solution. These processes are of special interest in terms of the mobility of toxic trace elements in groundwater and surface water systems [12]. Important remobilization processes include: (1) acidification, (2) competitive adsorption of other metal ions or anions, (3) reductive and non-reductive dissolution of the solid phase, and (4) complexation of metal ions by ligands [13]. The remobilization of metals by synthetic anthropogenic chelating agents has received much attention. The use of EDTA and NTA has especially been questioned because of their potential for increasing the solubilization and remobilization of heavy metals from aquatic sediments or from aquifer material during the infiltration from river water to ground water. EDTA has been measured in rivers at mean concentrations ranging from 0.01 to 0.1 $\mu$M with peak concentrations of up to 0.6 $\mu$M [14]. EDTA is not degraded during conventional wastewater treatment but is degraded in rivers by photolysis of the Fe(III) EDTA complex [15]. EDTA can increase the dissolved concentration of metal ions by two process: by dissolution of a solid phase (aluminium, iron, or manganese oxides) and by remobilization of adsorbed or precipitated metal ions like Cu, Zn, Pb, or Cd [12].

EDTA is commonly applied in several industries (household detergents, photographic industry, pharmacy, and textile and paper manufacture) to bind interfering or contaminating metal ions into inactive, cyclic metal complexes. Because EDTA is used in significant amounts and is a rather stable compound in wastewater-treatment plants and in the aquatic environment, the widespread usage of EDTA and similar ligands has raised considerable concern recently [16]. Therefore, it is of vital importance to have precise knowledge about the ecological risks, both direct and indirect, involved in their usage in different industrial applications as well as in household and agricultural applications [17]. The purposes of this study are to compare the remobilization ability of EDTA (under different concentrations and pH values), pH values (without EDTA), and metal EDTA complexes on some metals of representative sediment samples from River Nile, as well as to determine the variation in metal contents in five sediment factions (extractants) after leaching with EDTA. The metal ions studied were selected on the basis of their toxicities (Cd and Pb), in addition to industrial impact and relatively high concentrations with respect to Cu and Zn in the sediments. Many industries (metal alloys, pesticides, ceramic, dyes, and fertilizers) in the cities of the sampling sites and several industries (household detergents, photographic industry, pharmacy, textile, and paper manufacture) in these cities are responsible for EDTA discharge.

## 2. Materials and methods

### 2.1 *Sampling*

In the present study, sediment samples (0–15) were collected from the main stream of River Nile (Egypt) at two stations [Aswan city (the southern part of Nile) and Mansoura (the northern part of Nile, Damietta branch)] by means of a spring-loaded Ekman dredge sediment sampler made of stainless steel. Sediment samples collected at each sampling station (8 samples) were dried in air then in an electrical oven at 105° C for 48 h. The dried samples from each station were mixed well and formed into a cone shape. Subsequently, two opposite quarters were taken and the method was repeated until the sample was reduced to 500 g. A 200 g portion from each dried representative sample was sieved through a nylon sieve to yield a size fraction of $<63\,\mu$m (the fraction is imperative to base metal analyses). Each fraction was stored in a clean polyethylene bottle until needed for the experiments.

### 2.2 *Sequential extractions of selected heavy metals in leached and unleached sediments*

To determine the effect of EDTA on the metals in different fractions, the sequential extractions were carried out on the leached and unleached sediments. To obtain the leached sediments, 25 g of the $<63\,\mu$m soil fraction were shaken with 250 ml of 0.01 M EDTA solution for 6 h, then filtered through Whatman filter no. 42 paper and washed several times with deionized water. The leached sediment sample was dried at 105 °C for 24 h. The sequential extraction procedures [18–20] were as follows:

(1) *Exchangeable form.* One gram from each sediment sample was extracted using 25 ml of 1.0 M $MgCl_2$ (pH 7.0) by shaking for 1 h.
(2) *Carbonate bound form.* The residue from step (1) was leached using 25 ml of 1.0 M $CH_3COONa$ (pH 5.0) by shaking for 6 h.
(3) *Fe/Mn oxide bound form* (reducible phase). The residue from step (2) was extracted using 25 ml of 0.04 M $NH_2OH.HCl$ in 25% $CH_3COOH$ at 96 °C by shaking for 6 h.
(4) *Organic matter/sulphides bound form* (oxidized phase). The residue from step (3) was extracted using 25 ml of 30% $H_2O_2$ at 85 °C for 3 h.
(5) *Residual form.* The residue from step (4) was digested using a mixture of conc. $HNO_3$ (10 ml), $HClO_4$ (5 ml), and HF (10 ml) acids.

After each step, the separation of solid and solution was performed by centrifuging at 10 000 rpm for 20 min. The supernatant was removed by pipette, and the residual sediment was rinsed by deionized water and centrifuged again. The washing water was discarded. Metal concentrations in solutions were acidified with diluted $HNO_3$ acid and measured using flame atomic absorption spectrophotometry (FAAS).

### 2.3 *Effect of EDTA concentrations on the remobilization of metal ions*

Each 25 ml EDTA solution with different concentrations ($10^{-7}$, $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$, $10^{-2}$, and $10^{-1}$ mol/L) containing 3 g of sediment samples was placed in a 50 ml plastic bottle and shaken for 6 h at room temperature (the solutions were adjusted at pH 8, the mean pH value of River Nile water), then centrifuged for 20 min at 10 000 rpm. The supernatants were filtered though a Whatman filter no. 42 paper and acidified with diluted $HNO_3$ to pH 2 for the FAAS analyses.

**2.4** *Effect of pH values on the remobilization of metal ions*

To determine the effect of each factor (pH or EDTA) on the remobilization of metal ions from the sediment samples, two experiments were applied on the sediment samples (the release of metals as a function of pH only and the function of pH in the presence of EDTA). To determine the effect of pH values on the ability of EDTA to remobilize metal ions from sediments, 3 g of sediment sample and 25 ml of 0.01 M EDTA solution were placed into each 50 ml plastic bottle and adjusted to different pH values (from pH 1 to pH 8), shaken for 6 h, then centrifuged for 20 min at 10 000 rpm. Also, this experiment was carried out on the sediment samples without EDTA (bidistilled water only) at the same pH values. The supernatants were filtered through a Whatman filter no. 42 paper and acidified with diluted $HNO_3$ acid to pH 2 for the FAAS analyses.

**2.5** *Effect of M–EDTA complex with different concentrations on the remobilization of studied metal ions from sediment samples*

To investigate the influence of metal complexation by EDTA on metal-ion remobilization processes, for each experiment (20 experiments), 3 g from each sediment sample and 25 ml of each EDTA–metal complex (1:1 metal–EDTA complex (1:1 metal–EDTA complex, and the metal in nitrate form) solution (Ca–EDTA, Zn–EDTA, Pb–EDTA, Cd–EDTA and Cu–EDTA) with different concentrations (0.1, 1.0, 10, and 100 $\mu$M) were placed into a 50 ml polyethylene bottle and the mixture adjusted to pH 8. The suspensions were shaken for 6 h and centrifuged for 20 min at 10 000 rpm. The supernatant was then filtered through a Whatman filter no. 42 paper and acidified with dilute $HNO_3$ acid to pH 2 for the FAAS analyses.

**2.6** *Instrumental techniques*

Metal-ion concentrations (Cu, Zn, Cd, Pb, and Ca) in the different leachates and reference materials (two NIST standard soil materials, NIST SRM 2709 and NIST SRM 2711 [21] were determined by flame atomic absorption spectrophotometry (Model Solaar 969, ATI Unicam Comp.) equipped with a digital direct concentration read out and an air–acetylene burner. Single-element hollow-cathode lamps (ATI Unicam Comp.) and standard instrumental conditions were used for each element. To validate the method for accuracy and precision, certified reference materials were analysed for each element. Suitable precautions were taken to minimize interference when necessary. Background absorption can be troublesome, so the traditional and simplest methods are used to monitor absorbance of the continuum output of a deuterium lamp beam and to correct the analysed signal for any absorption detected.

**2.7** *Quality control*

Accurate analysis of heavy and toxic elements is dependent upon the prevention of element contamination. Quality control was achieved by analysing reference materials independently prepared from the standards. All chemicals used were purchased from DDH and E. Merck (A.R., 99.9%). All vessels were made of Pyrex and high-density polyethylene, washed with 30% $HNO_3$, then rinsed three times with bidistilled water. The accuracy of the methods was verified by subjecting standard reference material to the overall analytical procedures. Analysis of reference material yielded metal concentrations with acceptable limits. The precision of the results was estimated by triplicate analysis. The accuracy and precision of the results

were estimated as the standard deviation for three replicates of samples. Atomic-absorption-spectroscopic standard solutions (1 mg ml$^{-1}$) for the elements Cu, Zn, Cd, Pb, and Ca (BDH, UK) were prepared by diluting stock solutions using deionized water. The standard curves were verified after 10 successive runs by analysis of one standard solution within the linear range for each sample. All stages of samples preparation, analysis, and measurement were carried out in a clean environment.

## 3.  Results and discussion

### 3.1  *Sequential extractions of selected heavy metals in unleached sediments*

The mean metal ion concentrations (mean of eight samples for each site) in various geochemical phases in the sediment samples are shown in table 1. The major portion of most metals (figure 1) was bound to the residual fraction (Pb, 29.64–66.67% and Zn, 43.76–50.09% at Aswan and Mansoura, respectively, in addition to Cu, 72.34% and Cd, 52.94% at Mansoura). This observation indicates that most of the metals may come from the parent materials of geological origin and may exist in the residual form in the sediment. The residual fraction could be considered as an inert phase corresponding to the part of metal that cannot be mobilized and as the geochemical background values for the elements in the sediment [18]. Except for the residual phase, concentrations in the organic phase were generally the highest for Cu, 54.55–11.32% at Aswan and Mansoura, respectively, and Zn, 24.65% at Mansoura (figure 1a). A significant amount of Cu (72.34%) in Mansoura sediment was associated in the residual phase, presumably corresponding to copper held to minerals lattice or sorbed to the clays. This behaviour has also been reported by others [22, 23]. Beside the organic phase fraction, the reducible fraction (Fe/Mn oxides) was another dominant binding phase of Pb, Cd, Cu, and Zn (table 1). Copper could easily form complexes with organic matter due to the high stability constant of organic–Cu compounds [24–26]. The association of Zn with Fe–Mn oxides in sediment and soils has been widely recognized [27, 28]. The main mechanisms of anthropogenic Zn accumulation in the top layers of sediment may be related to precipitation and coprecipitation with Fe/Mn oxides and complexation with organic matter [29]. Zinc compounds are usually used for wheel manufacture, metal alloys, pesticides, and ceramic and plastic moulding. Some ores such as phosphate and materials used for cement manufacture may contain zinc minerals. Therefore, a high concentration of Zn would be expected in soil, plants, and air particulates of the surrounding environment [30]. The concentrations of Pb, Zn and Cu bound to the Fe–Mn oxide fraction had a significant correlation with reducible Mn concentration. The Pb in the Fe–Mn oxide fraction was also related to reducible Fe, but no significant relationship was found between the concentration of Zn and Cu bound to the Fe–Mn oxide and reducible Fe. This suggests that Mn oxides can play an important role in binding these metals in the sediments [29]. Oakley *et al*. [31] reported that hydrous Mn oxides exhibited a more extensive isomorphic substitution than amorphous Fe oxides and showed higher conditional equilibrium constants for the heavy metals than Fe oxides. Pb can form stable complexes with Fe and Mn oxides [27, 32]. The Pb bound to the non-residual fractions showed higher concentrations (70.36%) in the Aswan samples than Mansoura samples (33.33%). This is attributed to the effluent of gasoline exhausts or spills from the tourist river crafts. The crafts running on gasoline containing tetramethyl lead. Lead is deposited on and adsorbed on the mud bed [33]. Also, the high concentrations of Pb at Aswan may be attributed to the weathering of igneous rocks containing high levels of Pb [34]. A considerable amount of Pb bound to the carbonate phase fraction (21.76%) was measured in Aswan sediment samples (figure 1a). This maybe reflects the geomorphology of this region. The dominant rocks of western side of River Nile

Table 1.  Sequential fractions of some heavy metals ($\mu g\,g^{-1}$, mean of three readings) in unleached river Nile sediment samples (mean of eight samples from each site).

| | Metals | | | | | | | |
| | Cu | | Zn | | Cd | | Pb | |
| Fractions | A | M | A | M | A | M | A | M |
|---|---|---|---|---|---|---|---|---|
| Exchangeable | $0.42 \pm 0.05$ | $0.42 \pm 0.04$ | $5.83 \pm 0.41$ | $1.42 \pm 0.09$ | UD | UD | $0.42 \pm 0.05$ | $0.25 \pm 0.01$ |
| Carbonate | $1.41 \pm 0.15$ | $0.25 \pm 0.02$ | $1.34 \pm 0.11$ | $13.16 \pm 0.11$ | UD | UD | $1.16 \pm 0.08$ | $0.33 \pm 0.04$ |
| Reducible | $1.92 \pm 0.16$ | $1.25 \pm 0.09$ | $1.41 \pm 0.15$ | $9.59 \pm 1.10$ | $0.08 \pm 0.02$ | $0.08 \pm 0.01$ | $1.50 \pm 0.09$ | $1.17 \pm 0.07$ |
| Organic | $6.00 \pm 0.44$ | $1.33 \pm 0.10$ | $0.84 \pm 0.65$ | $23.58 \pm 1.90$ | $0.09 \pm 0.01$ | UD | $0.67 \pm 0.06$ | $0.50 \pm 0.06$ |
| Residual | $1.25 \pm 0.11$ | $8.50 \pm 0.74$ | $7.33 \pm 0.80$ | $47.92 \pm 4.10$ | UD | $0.09 \pm 0.01$ | $1.58 \pm 0.10$ | $4.50 \pm 0.31$ |

*Note*: UD: under the detection limit; A: Aswan sediment; M: Mansoura sediment.
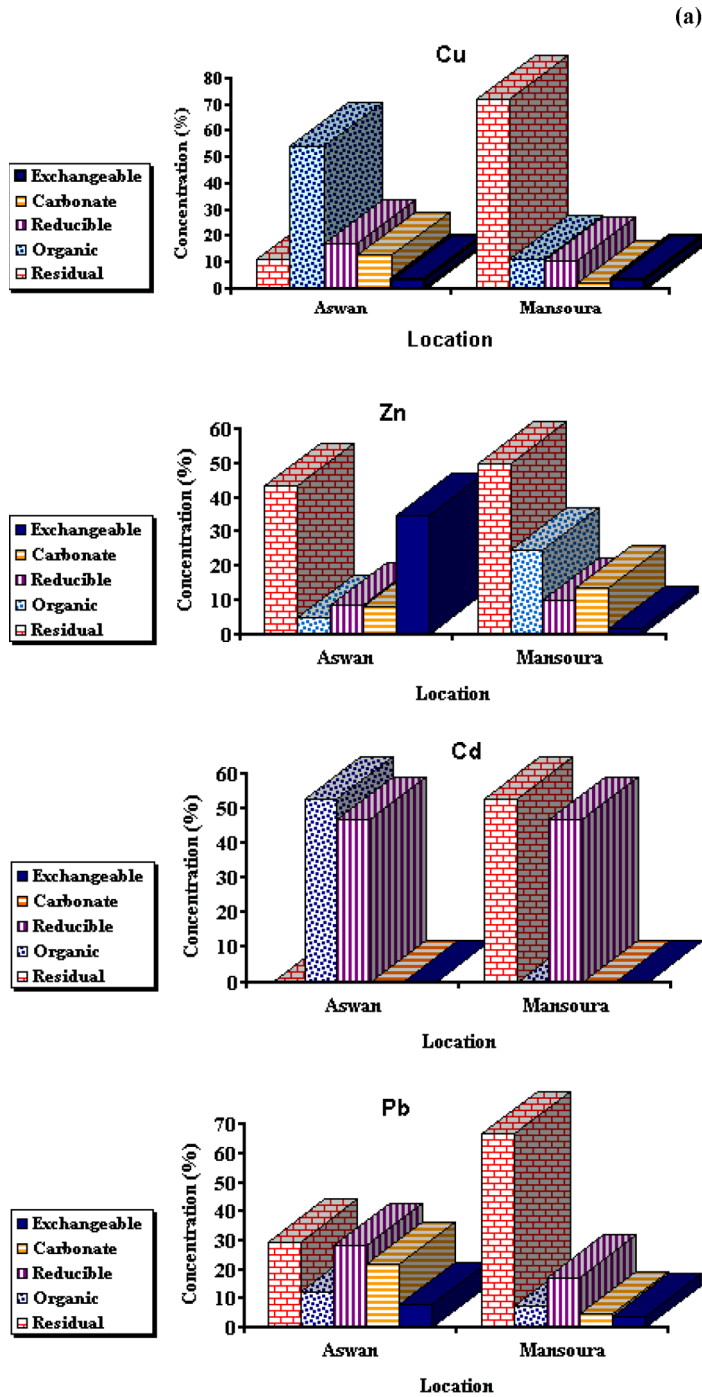
**(a)**



Figure 1.    (a) Distribution of some metal concentrations (%) in the unleached sediment samples between the different extraction phases. (b) Distribution of several metal concentrations (%) in the leached (0.1 M Na–EDTA) sediment samples between the different extraction phases.
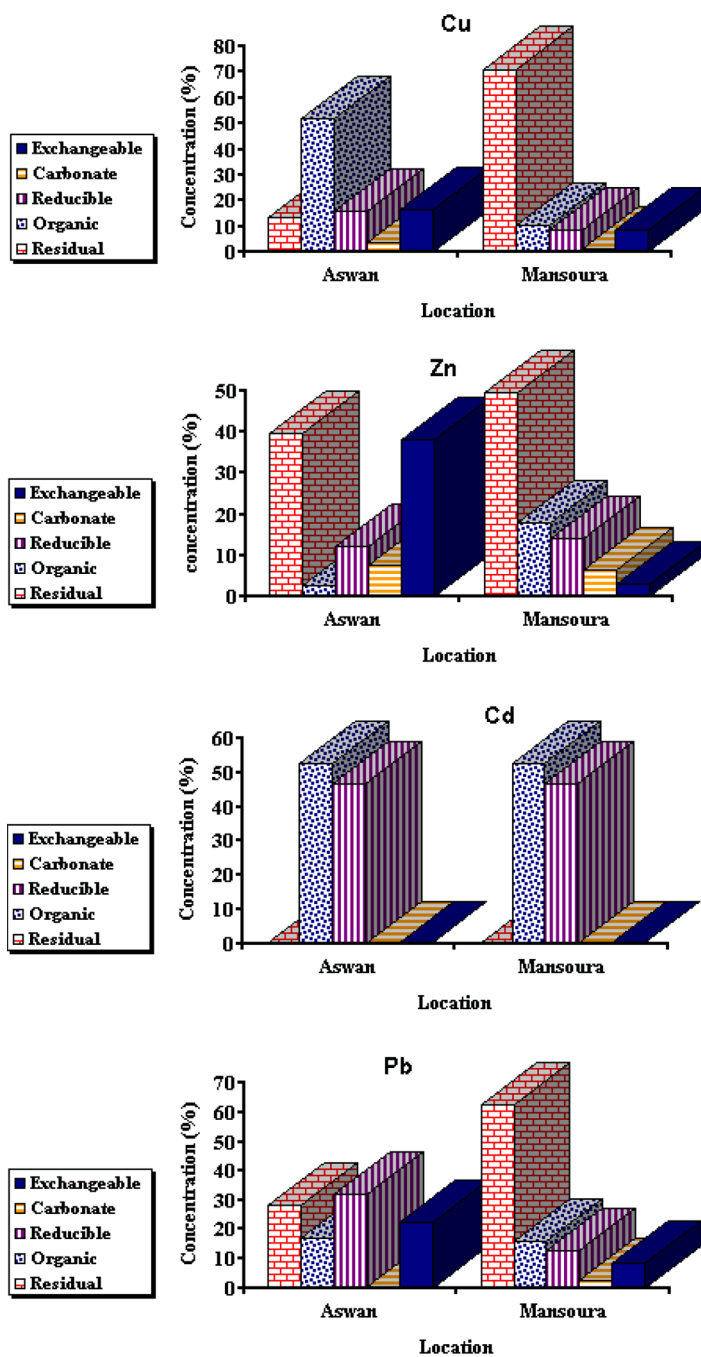
*M. E. Soltan*

**(b)**



Figure 1.   Continued.

are Nubian sandstone, limestone, dolomite, and kaoline, whereas these rocks are rich in Ca and Mg carbonates. A number of studies have found that Pb can be associated with carbonates [32, 35]. Carbonate can be an important absorbent for Pb when organic matter and Fe–Mn oxides are less abundant in the aquatic system. The carbonate form is a loosely bound phase and liable to change with environmental conditions [29]. Increases in Cu, Pb, and Zn bound to the residual fraction in the Mansoura sediment (72.34%, 66.67%, and 50.09%, respectively) rather than the Aswan samples may be attributed to solid waste from the factories situated in this region.

### 3.2 *Sequential extractions of heavy metals in leached sediments*

Sequential extraction was used in this step to evaluate any changes in metal ion concentrations in different fractions after leaching with EDTA (0.01 M Na–EDTA). As expected, an obvious effect on the distribution of the metals between the different fractions in the sediment samples was detected after this process (table 2 and figure 1b). The concentration of Cu increased in the exchangeable fraction in Aswan (from $0.42 \pm 0.05$ to $1.52 \pm 0.10 \, \mu g \, g^{-1}$) and Mansoura (from $0.42 \pm 0.04$ to $0.75 \pm 0.06 \, \mu g \, g^{-1}$) sediment samples and decreased in carbonate, reducible, and organic fractions, and to a lesser extent in the residual fraction ($1.25 \pm 0.11$ to $1.24 \pm 0.04$ and $8.5 \pm 0.74$ to $6.17 \pm 0.32 \, \mu g \, g^{-1}$ in the Aswan and Mansoura samples, respectively). The principal worldwide anthropogenic sources of Cu are metal extraction and industrial use such as pesticide and dye industries, waste incineration, and oil combustion [30]. Zn content showed a clear increase in exchangeable ($5.83 \pm 0.41$ to $6.27 \pm 0.27$ and $1.42 \pm 0.09$ to $2.5 \pm 0.12 \, \mu g \, g^{-1}$ in Aswan and Mansoura samples, respectively) and reducible ($1.41 \pm 0.15$ to $2.0 \pm 0.40$ and $9.59 \pm 1.10$ to $11.33 \pm 1.20 \, \mu g \, g^{-1}$ in Aswan and Mansoura samples) fractions, but a decrease in carbonate, organic, and, to a lesser extent, residual fractions. Also, Pb showed a similar behaviour, exhibiting a remarkable increase in exchangeable and organic fractions in the two sediment samples but a decrease in carbonate and reducible fractions. No change in the concentration of cadmium before and after leaching by EDTA, where its concentrations under detection limits in exchangeable and carbonate fractions, while its concentration in residual form changed to the reducible form after leaching by EDTA (Mansoura samples) changed to reducible fraction. These results are consistent with the hypothesis of Sun *et al.* [36]. The decrease in metal concentrations in most fractions reflects the ability of EDTA to remove the metals from these fractions, and it is difficult to generalize as to which fraction was more mobile than the others.

### 3.3 *Effect of EDTA concentrations on the remobilization of metal ions from the sediment samples*

The remobilization of investigated metal ions by different EDTA concentration is depicted in table 3. The release of metal ions was studied at pH 8, a pH corresponding to natural aquatic conditions. The metal concentrations are directly proportional to the EDTA concentration, suggesting remobilization by formation of an M–EDTA complex. There is clear increase in Cu and Zn remobilization with increasing of EDTA concentrations ($0.18 \pm 0.05$ and $0.17 \pm 0.02 \, \mu g \, g^{-1}$ for Cu with $10^{-7}$ M increasing to $14.08 \pm 2.40$ and $4.67 \pm 0.55 \, \mu g \, g^{-1}$ with $10^{-1}$ M in addition to $0.58 \pm 0.07$ and $0.50 \pm 0.09 \, \mu g \, g^{-1}$ for Zn to $19.75 \pm 1.20$ and $14.47 \pm 0.75 \, \mu g \, g^{-1}$ with the above EDTA concentrations). Pb was only slightly influenced ($0.58 \pm 0.06$ and $0.33 \pm 0.02 \, \mu g \, g^{-1}$ with the lowest EDTA dose and $6.17 \pm 0.58$ and $1.5 \pm 0.09 \, \mu g \, g^{-1}$).

Cd remobilization by EDTA appeared to be independent of the EDTA concentration, the remobilized Cd ($0.08 \pm 0.01 \, \mu g \, g^{-1}$) with lowest EDTA concentration ($10^{-7}$ M) equal the

Table 2.  Sequential fractions of some heavy metals ($\mu g\, g^{-1}$, mean of three readings) in leached (0.01 M Na–EDTA) river Nile sediment samples (mean of eight samples from each sites).

| Fractions | Metals | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Cu | | Zn | | Cd | | Pb | |
| | A | M | A | M | A | M | A | M |
| Exchangeable | $1.52 \pm 0.10$ | $0.75 \pm 0.06$ | $6.27 \pm 0.027$ | $2.5 \pm 0.12$ | UD | UD | $1.08 \pm 0.08$ | $0.38 \pm 0.04$ |
| Carbonate | $0.34 \pm 0.03$ | $0.12 \pm 0.02$ | $1.25 \pm 0.09$ | $5.17 \pm 0.33$ | UD | UD | $0.02 \pm 0.01$ | $0.12 \pm 0.02$ |
| Reducible | $1.50 \pm 0.11$ | $0.75 \pm 0.05$ | $2.00 \pm 0.11$ | $11.33 \pm 1.2$ | $0.08 \pm 0.01$ | $0.08 \pm 0.02$ | $1.57 \pm 0.08$ | $0.55 \pm 0.03$ |
| Organic | $4.83 \pm 0.21$ | $0.88 \pm 0.06$ | $0.41 \pm 0.03$ | $14.58 \pm 1.5$ | $0.09 \pm 0.01$ | $0.09 \pm 0.01$ | $0.83 \pm 0.05$ | $0.72 \pm 0.08$ |
| Residual | $1.24 \pm 0.04$ | $6.17 \pm 0.32$ | $6.50 \pm 0.41$ | $40.17 \pm 3.6$ | UD | UD | $1.37 \pm 0.09$ | $2.83 \pm 0.14$ |

*Note*: UD: under the detection limit; A: Aswan sediment; M: Mansoura sediment.

Table 3. Effect of EDTA concentrations on the remobilization of some heavy metals ($\mu g\, g^{-1}$, mean of three readings) from the sediment samples (mean of eight samples from each site) at pH 8.

| EDTA (M) | Metals | | | | | | | |
| | Cu | | Zn | | Cd | | Pb | |
| | A | M | A | M | A | M | A | M |
|---|---|---|---|---|---|---|---|---|
| $10^{-7}$ | $0.18 \pm 0.05$ | $0.17 \pm 0.02$ | $0.58 \pm 0.07$ | $0.50 \pm 0.09$ | UD | $0.08 \pm 0.01$ | $0.58 \pm 0.06$ | $0.33 \pm 0.02$ |
| $10^{-6}$ | $0.28 \pm 0.09$ | $0.17 \pm 0.02$ | $0.88 \pm 0.14$ | $0.92 \pm 0.09$ | $0.08 \pm 0.01$ | $0.08 \pm 0.01$ | $0.25 \pm 0.03$ | $0.42 \pm 0.05$ |
| $10^{-5}$ | $0.43 \pm 0.13$ | $0.17 \pm 0.03$ | $0.87 \pm 0.13$ | $1.08 \pm 0.08$ | $0.08 \pm 0.01$ | $0.08 \pm 0.01$ | $0.50 \pm 0.04$ | $0.43 \pm 0.04$ |
| $10^{-4}$ | $0.50 \pm 0.08$ | $0.17 \pm 0.02$ | $1.42 \pm 0.20$ | $1.15 \pm 0.07$ | $0.08 \pm 0.01$ | $0.08 \pm 0.02$ | $0.50 \pm 0.05$ | $0.58 \pm 0.05$ |
| $10^{-3}$ | $2.33 \pm 0.31$ | $1.00 \pm 0.06$ | $3.00 \pm 0.45$ | $1.42 \pm 0.14$ | $0.08 \pm 0.01$ | $0.08 \pm 0.01$ | $0.50 \pm 0.06$ | $0.59 \pm 0.07$ |
| $10^{-2}$ | $4.16 \pm 0.59$ | $1.50 \pm 0.09$ | $14.17 \pm 1.54$ | $7.25 \pm 0.86$ | $0.08 \pm 0.01$ | $0.09 \pm 0.02$ | $4.58 \pm 0.34$ | $0.59 \pm 0.05$ |
| $10^{-1}$ | $14.08 \pm 2.4$ | $4.67 \pm 0.55$ | $19.75 \pm 1.2$ | $14.47 \pm 0.95$ | $0.08 \pm 0.01$ | $0.09 \pm 0.01$ | $6.17 \pm 0.58$ | $1.50 \pm 0.09$ |

*Note*: UD: under the detection limit; A: Aswan sediment; M: Mansoura sediment.

Table 4.   Theoretically maximum capacity of $0.1\,\mu M$ Na–EDTA to desorb some metals from sediments into aquatic phase and stability constants of metal–EDTA.

| Stability constant ($\log K$) | Desorption capacity | Metal ($\mu g\,g^{-1}$) |
|---|---|---|
| 16.3 | 2.7 | Al |
| 10.7 | 4.0 | Ca |
| 16.6 | 11.2 | Cd |
| 18.8 | 8.4 | Cu |
| 25.1 | 5.6 | Fe |
| 21.9 | 20.1 | Hg |
| 18.6 | 5.9 | Ni |
| 18.0 | 20.7 | Pb |
| 16.7 | 6.5 | Zn |

same remobilized amount by the highest concentration ($10^{-1}$ M). This pattern suggests that EDTA first scavenges the Cu and Zn-complexable pool and that surplus chelator molecules move to the next available metal [8]. Generally, the low concentration of remobilized metals due to the pH of solution (pH 8), whereas the solubility of the metal compounds is very low in quite a wide range of OH (from 7 to 14), but dramatically increases in the acid (pH < 5) medium [37]. The heavy metals were easily remobilized under the complexing action of EDTA can, however, also solubilize some of the sediment constituents (e.g. Fe oxide) [38]. The rest of the Cu, Cd, and Pb which is not remobilizable under these conditions (pH and presence of EDTA in excess), is most likely more strongly or differently associated with sediment (e.g. part of the crystalline matrix) [39]. The low concentration of remobilized metals in the presence of EDTA with low concentrations ($<10^{-4}$) was explained by the low concentration of the ligand compared with the remobilizable metals [39]. In the presence of high concentrations of heavy metals in the sediments, EDTA is known to form chelates with metals at a molar ratio of 1:1, and so the quantity of these compounds which can theoretically desorb trace metals can be calculated (table 4), i.e. the amount of metal that the free anionic form of complexing agent is able to desorb to the water phase. Thus, ecological risk against drainage of EDTA solutions via industrial wastewater or any effluents to the river stream. In addition, the most toxic metals (Cd, Pb, Hg, etc.) can be remobilized to a more significant extent than other metals (table 4). Also, the metal-complex stability constants of these extremely toxic non-essential metals are high, and thus their desorptions are compatible on a thermodynamical basis when metal-chelated EDTA is in contact with sedimented material [17].

## 3.4   *Effect of pH values on the remobilization of metal ions*

### 3.4.1   **pH-dependent metal-ion remobilization by distilled water.**   The remobilization of metal ions as a function of pH exhibited easily remobilized for Zn (for example, 46.31 and $32.32\,\mu g\,g^{-1}$ at pH 1 in Aswan and Mansoura sediments, respectively) followed by Cu (5.33 and $1.58\,\mu g\,g^{-1}$ in the same samples) and Pb (2.21 and $1.50\,\mu g\,g^{-1}$ at the same sites and the same pH value). Cd ($0.08\,\mu g\,g^{-1}$ in Aswan and sediment samples at pH 1) was the least easily remobilized. This behaviour depends on the affinity between the metal and the solid surface, and the metal content and its form in the sediment, in addition to the relation between the surface complexation constants and the hydrolysis constants of metals [40] according to the following equation:

$$M(H_2O)_x^{n+} \longleftrightarrow MOH(H_2O)_{x-1}^{(n-1)+} + H^+.$$

Table 5.   pH-dependent metal remobilization ($\mu$g g$^{-1}$, mean of three readings) by bidistilled water from the sediment samples (mean of eight samples from each site).

| | Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cu | | Zn | | Cd | | Pb | |
| EDTA (M) | A | M | A | M | A | M | A | M |
| 1 | 5.33 ± 0.44 | 1.58 ± 0.20 | 46.31 ± 5.12 | 32.32 ± 2.54 | 0.08 ± 0.01 | 0.08 ± 0.01 | 2.21 ± 0.18 | 1.50 ± 0.12 |
| 2 | 0.17 ± 0.03 | 1.30 ± 0.11 | 12.41 ± 1.50 | 15.41 ± 1.95 | 0.16 ± 0.02 | 0.08 ± 0.02 | 1.51 ± 0.18 | 1.01 ± 0.09 |
| 3 | 0.17 ± 0.03 | 0.50 ± 0.04 | 18.33 ± 2.02 | 14.47 ± 1.05 | 0.16 ± 0.02 | 0.08 ± 0.01 | 0.35 ± 0.03 | 0.31 ± 0.04 |
| 4 | 0.17 ± 0.02 | 0.50 ± 0.05 | 17.91 ± 2.10 | 32.24 ± 2.80 | 0.16 ± 0.03 | 0.16 ± 0.03 | 0.35 ± 0.03 | 0.13 ± 0.03 |
| 5 | 0.25 ± 0.03 | 0.50 ± 0.03 | 22.32 ± 1.85 | 10.25 ± 1.15 | 0.08 ± 0.02 | 0.08 ± 0.01 | 0.28 ± 0.03 | 0.05 ± 0.01 |
| 6 | 0.17 ± 0.02 | 0.42 ± 0.04 | 7.75 ± 0.45 | 0.67 ± 0.05 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.18 ± 0.02 | 0.03 ± 0.01 |
| 7 | 0.83 ± 0.07 | 0.67 ± 0.05 | 11.50 ± 0.95 | 0.58 ± 0.07 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.18 ± 0.02 | 0.01 ± 0.01 |
| 8 | 0.92 ± 0.10 | 0.62 ± 0.07 | 0.33 ± 0.05 | 0.50 ± 0.06 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.16 ± 0.02 | 0.01 ± 0.01 |

*Note*: A: Aswan sediment; M: Mansoura sediment.

Table 6. pH-dependent metal remobilization ($\mu$g g$^{-1}$, mean of three readings) by Na–EDTA ($10^{-2}$ M l$^{-1}$) from the sediment samples (mean of eight samples from each site).

| EDTA (M) | Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cu | | Zn | | Cd | | Pb | |
| | A | M | A | M | A | M | A | M |
| 1 | 5.92 ± 0.75 | 2.42 ± 0.18 | 85.54 ± 7.10 | 45.74 ± 6.05 | 0.08 ± 0.01 | 0.08 ± 0.02 | 6.70 ± 0.90 | 2.08 ± 0.18 |
| 2 | 1.00 ± 0.08 | 1.92 ± 0.15 | 27.57 ± 2.10 | 38.82 ± 4.05 | 0.08 ± 0.01 | 0.08 ± 0.01 | 6.50 ± 0.75 | 1.67 ± 0.20 |
| 3 | 1.00 ± 0.08 | 0.88 ± 0.06 | 12.83 ± 1.08 | 11.08 ± 1.20 | 0.08 ± 0.01 | 0.08 ± 0.01 | 6.55 ± 0.80 | 0.92 ± 0.70 |
| 4 | 1.00 ± 0.08 | 0.78 ± 0.07 | 16.74 ± 1.12 | 10.25 ± 1.45 | 0.16 ± 0.02 | 0.08 ± 0.01 | 5.33 ± 0.70 | 0.50 ± 0.30 |
| 5 | 0.92 ± 0.10 | 0.62 ± 0.07 | 15.08 ± 1.15 | 7.25 ± 0.58 | 0.16 ± 0.02 | 0.08 ± 0.02 | 5.33 ± 0.65 | 0.50 ± 0.04 |
| 6 | 0.92 ± 0.08 | 0.58 ± 0.07 | 13.91 ± 1.60 | 9.83 ± 0.95 | 0.08 ± 0.01 | 0.08 ± 0.02 | 4.91 ± 0.60 | 0.67 ± 0.07 |
| 7 | 1.33 ± 0.11 | 0.87 ± 0.05 | 13.50 ± 0.09 | 9.58 ± 1.10 | 0.08 ± 0.01 | 0.08 ± 0.01 | 4.17 ± 0.55 | 0.50 ± 0.04 |
| 8 | 1.00 ± 0.11 | 0.91 ± 0.06 | 13.00 ± 1.15 | 8.50 ± 1.05 | 0.08 ± 0.01 | 0.08 ± 0.02 | 4.17 ± 0.40 | 0.42 ± 0.04 |

*Note*: A: Aswan sediment; M: Mansoura sediment.

Also, the results (table 5) show that the remobilized content of metal ions at acidic pH values was more than the slight acidic (at pH 5, the remobilized Zn; $22.32–10.25 \, \mu g \, g^{-1}$, Cu; $0.25–0.50 \, \mu g \, g^{-1}$ and Pb; $0.28–0.05 \, \mu g \, g^{-1}$ in Aswan and Mansoura sediments, respectively) and alkaline (at pH 8, the remobilized Zn; $0.33–0.50 \, \mu g \, g^{-1}$, Cu; $0.92–0.62 \, \mu g \, g^{-1}$ and Pb; $0.16–0.01 \, \mu g \, g^{-1}$ in Aswan and Mansoura sediments, respectively) conditions, because the high concentrations of $H_3O^+$ could effectively complete with the metal ion for adsorption sites [41].

### 3.4.2 pH-dependent metal remobilization by EDTA ($10^{-2}$ M).

The metals were greatly remobilized under the complexing action of EDTA (this observation is clear by comparing table 5 with table 6), thus showing that some of these elements were adsorbed on the sediment
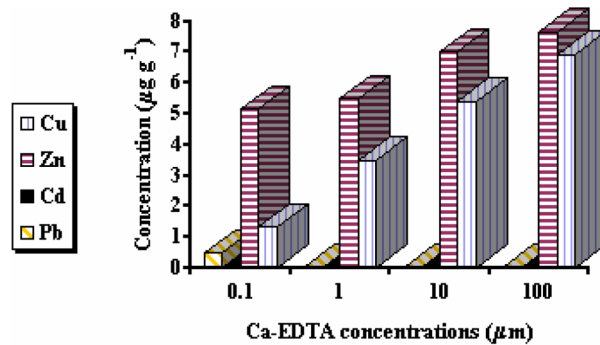


Figure 2. Remobilization rate of metals ($\mu g \, g^{-1}$) from sediment samples by different concentrations of Ca–EDTA complex.
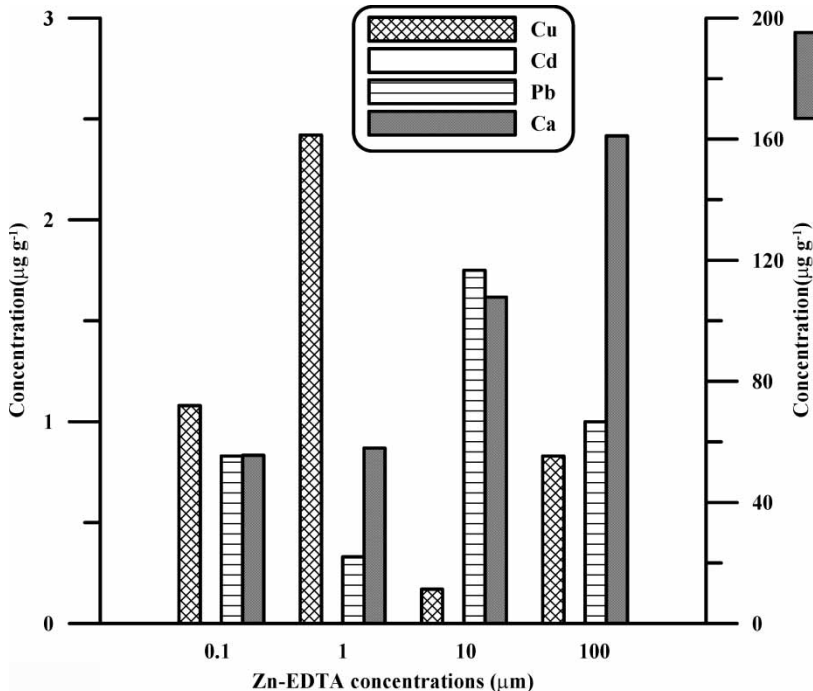


Figure 3. Remobilization rate of metals ($\mu g \, g^{-1}$) from sediment samples by different concentrations of Zn–EDTA complex.

[39]. EDTA can, however, also solubilize some of the sediment constituents, i.e. Fe oxides [38]. The metal extracted from sediment samples by EDTA would increase with decreasing pH (table 6). Some results in table 5 do not obey the previous observation. These results show that the concentrations of Cu at pH 7 ($1.33\,\mu g\,g^{-1}$) and pH 8 ($1.0\,\mu g\,g^{-1}$) in the Aswan samples and at pH 8 ($0.91\,\mu g\,g^{-1}$) in the Mansoura samples were higher than the concentrations at low pH values. Also, the behaviour of Pb at pH 6 ($0.67\,\mu g\,g^{-1}$) in Mansoura sediment samples is similar to this trend. This is attributed to the higher competition abilities of these chelating agents than the binding sites of sediment fractions at neutral pH conditions [7].

## 3.5 *Effect of metal–EDTA complex on the remobilization of metal ions from sediments*

In natural waters, EDTA is present almost exclusively in the form of a metal complex. Therefore, remobilization of metals is always a metal–metal–EDTA exchange reaction [12]. For example, it is shown that Fe (III)–EDTA introduced into river water is exchanged to Ca–EDTA at equilibrium, which takes time [42]. A relatively recent report [43] suggests that exchange reactions between Fe (III)–EDTA and both adsorbed and aquatic metals, such as Pb, Cd, and Zn, do occur at pH > 7, causing significant remobilization of trace metals at peak concentrations of EDTA. However, under acidic conditions, desorption of metals by EDTA does not occur. According to the above statement, the River Nile environment
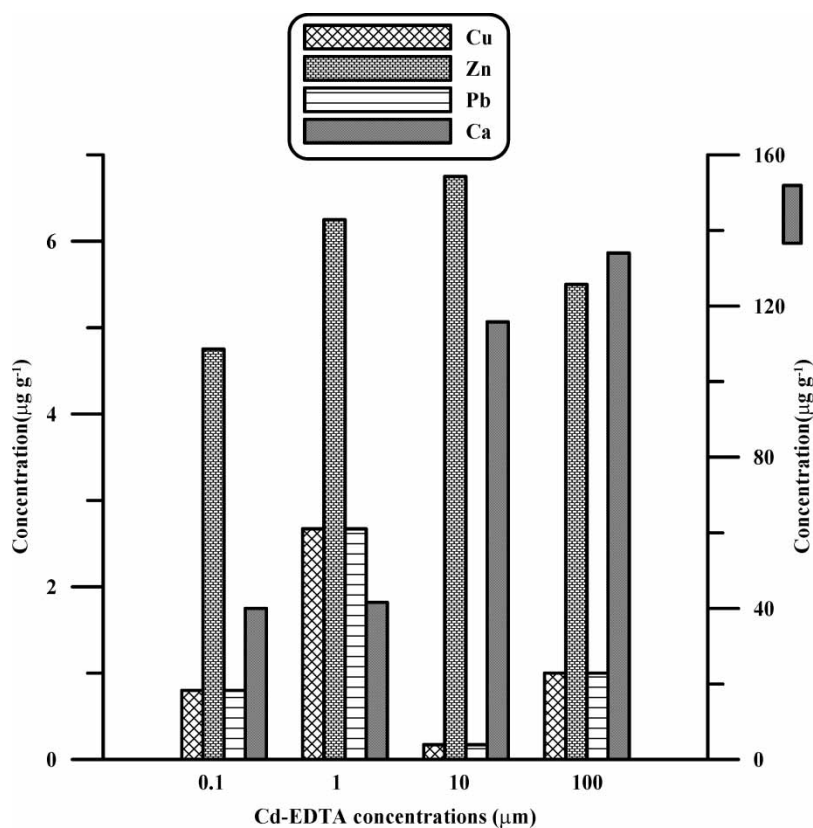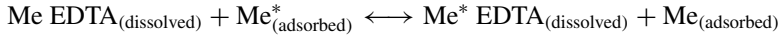


Figure 4.  Remobilization rate of metals ($\mu g\,g^{-1}$) from sediment samples by different concentrations of Cd–EDTA complex.

(pH 7.5–8.5) is suitable for the exchange reactions. The systematic of these reactions as follows:

$$Me\ EDTA_{(dissolved)} + Me^*_{(adsorbed)} \longleftrightarrow Me^*\ EDTA_{(dissolved)} + Me_{(adsorbed)}$$

The remobilization of dissolved metal ions by the EDTA–metal complex in these experiments depends on the kind of metal–EDTA complex and its concentration. The of Aswan and Mansoura sample sediment exhibited a similar trend for the remobilization of metal ions using the same metal–EDTA complex. The concentration of remobilized metals proportional to the concentration of the metal–EDTA complex (figure 2), but not with the same ratio, may be due to the low metal content in the sediment compared with the high concentrations of the metal–EDTA complex or may be due to the metal–EDTA complex consumed for the exchange reaction with other metals not studied in this work (for example, Mg, Fe, and Mn, which have high concentrations in the Nile sediment samples). The stoichiometric excess of calcium and magnesium at seawater concentrations has been shown to decrease significantly the rate of heavy-metal complexation by EDTA [44]. The remobilization rate of metals was dependent upon the added metal–EDTA complex, the exchange rate in the order Ca–EDTA (figure 2) > Zn–EDTA (figure 3) > Cd–EDTA (figure 4) > Cu–EDTA (figure 5) > Pb–EDTA (figure 6), due to the stability constant of metal–EDTA (log $K$ values for the previous complexes are 10.7, 16.7, 16.6, 18.8, and 18, respectively).
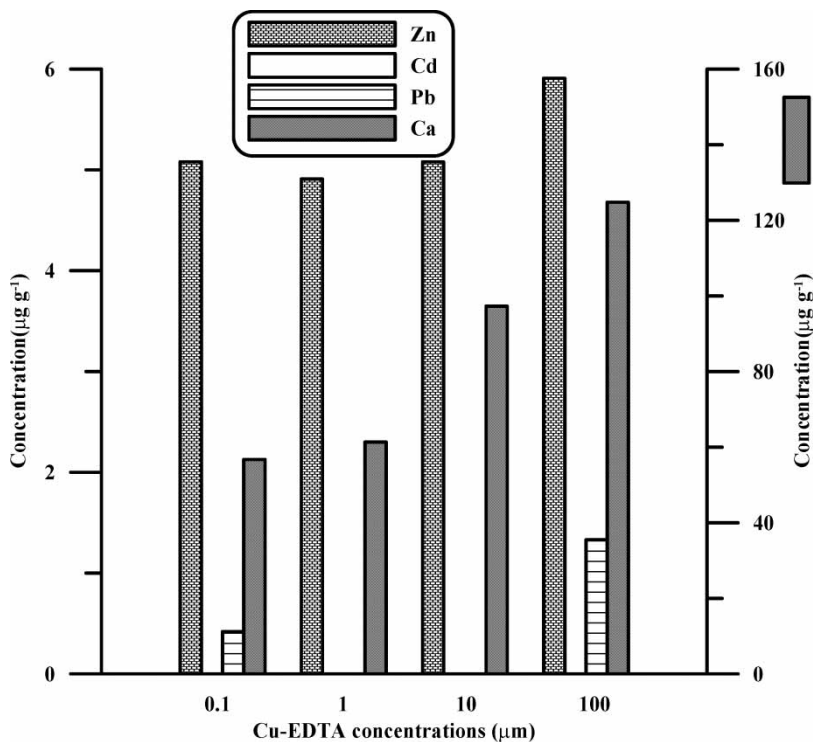


Figure 5. Remobilization rate of metals ($\mu g\ g^{-1}$) from sediment samples by different concentrations of Cu–EDTA complex.
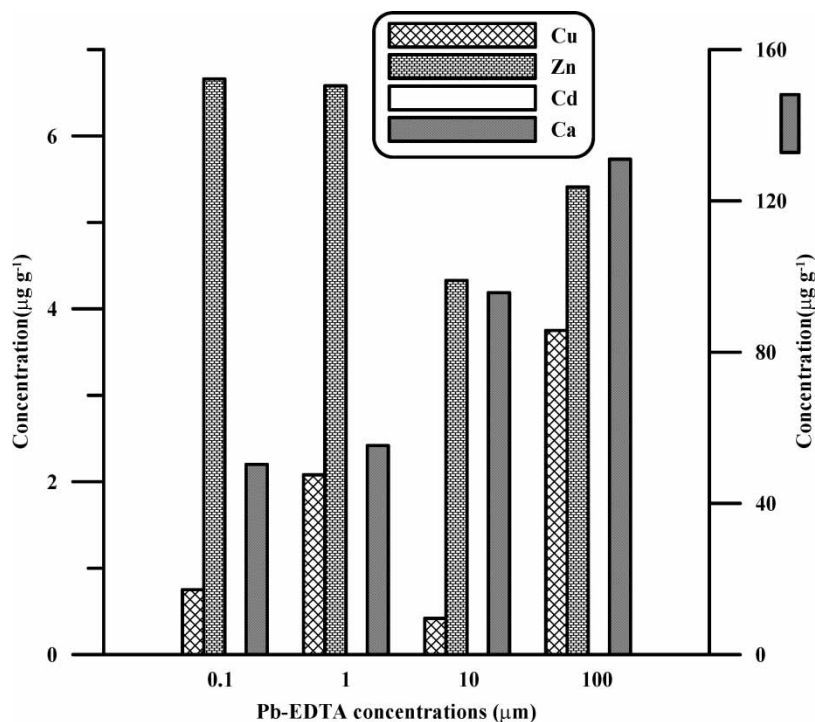
Figure 6. Remobilization rate of metals ($\mu$g g$^{-1}$) from sediment samples by different concentrations of Pb–EDTA complex.

## 4. Conclusion

In this paper, an experiment was designed to determine the effect of EDTA within industrial discharges on the remobilization of selected metal ions in the River Nile sediments. Sequential extractions are carried out on the leached (using EDTA solution) and unleached sediment samples to determine the effect of EDTA on the metals in different fractions. The ability of EDTA to remobilize selected metal ions from the sediment samples was studied as a function of the operating conditions, concentrations of EDTA, pH, and metal–EDTA complexes. Most of the metal contents in River Nile sediments bound to the residual fractions, followed by an organic phase (Cu, Cd, and Zn) and reducible fraction (Pb, Cd, Cu, and Zn). The considerable amount of Pb content in Aswan sediments (residual and carbonate fractions) reflects the geomorphology of this region and human activities (effluents of gasoline exhausts or spills from the tourist river crafts). The metals content in the sediment samples after leaching with EDTA solution showed a clear increase in the exchangeable fraction and decrease in the other fractions, indicating the role of EDTA in remobilization of metal ions from non-exchangeable fractions. The remobilized metal ions are directly proportional to the EDTA concentrations, suggesting remobilization by formation of the M–EDTA complex. The results indicated that EDTA first scavenges the Cu and Zn-complex pool and that surplus chelator molecules move to the next available metal. Also, the remobilized content of the metals studied using EDTA would increase with decreasing pH. The remobilization of metals is always a metal–metal–EDTA exchange reaction. At pH above 7, M–EDTA complex is exchanging with other adsorbed and dissolved metals, causing significant remobilization of trace metals at peak EDTA concentrations. However, under acidic conditions, desorption of metals by EDTA does not occur.

Thus, the environment of River Nile water (pH 7.5–8.5) is suitable for the exchange reactions. The results of the experiments demonstrated that the metals are greatly remobilized under the complexing action of EDTA when it is present in excess. Thus, all precautions must be taken to prevent any wastewater containing EDTA or any chelating agents discharging directly or indirectly via the River Nile stream, and because most of the EDTA remains in the aquatic phase, we have to take into account the ability of this portion to remobilize metal ions from sediments.

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