

## COPPER AND MANGANESE FORMS IN LAKE EDKU SEDIMENTS, ALEXANDRIA, EGYPT

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**ABSTRACT:** Lake Edku is one of the Nile Delta lakes. It is subjected to contaminations by several anthropogenic materials such as trace elements and other wastes. The distribution of the different chemical forms of copper and manganese has been studied using sequential extraction techniques. Chemical analysis of the sediments shows that CaCO<sub>3</sub> ranged from 3.7% to 9.6% and organic matter from 3.06% to 8.11%. The results indicate that the distribution of manganese among the six chemical forms in the sediments of the lake obeys the following order: Mn-residual > Mn-carbonate > Mn-moderately reducible > Mn-organic form > Mn-exchangeable > Mn-easily reducible fraction. Also, the data revealed that more than 50% of the total manganese was found in the residual form, while the remainder was distributed among the other forms. In contrast, more than 70% of the total copper content was associated with the five chemical forms (exchangeable, carbonate, easily and moderately reducible and organic forms).

Generally, the enrichment of manganese in the residual form revealed the important role in building up of clay minerals, while the distribution of copper among the different forms reflects an important role in biological and biochemical processes.

**KEY WORDS:** Copper, manganese, chemical forms, sediments.

### INTRODUCTION

Lake Edku is one of the Nile Delta brackish water coastal lakes. It is connected with the Mediterranean Sea through Boughaz El-Maadia (Fig. 1), and has an average depth of about 1m. The eastern region of the Lake receives considerable volumes of agricultural drainage water through three main drains (Edku, Bousily and Barzik). In contrast the western basin receives seawater from Abu-Qir Bay only during autumn and winter. The lake sediment is mixed with clay, silt and sand (El Sayed., 1993). For years, sequential extraction procedures have been developed and applied to extract from sediment under different conditions. Okbah (2001) studied the effect of sediment sample drying on the behavior of copper and manganese forms by sequential extraction technique, for all the sediment samples, extractable Cu and Mn at the five fractions were affected by the drying conditions due to the change in the original association of trace metals within the different sediment components. Many scientists have tried to differentiate residual (lithogenous origin) and non-residual (non-lithogenous origin) fractions of trace elements in soil and sediment.

The non-residual element fractions such as exchangeable, carbonates, iron and manganese oxides, and organics can be separated by using sequential extraction techniques (Gibbs, 1973, Gupta and Chen, 1975, Tessier *et al.*, 1979, Förstner *et al.*, 1981, Shuman, 1985, Okbah and Tayel, 1997,).

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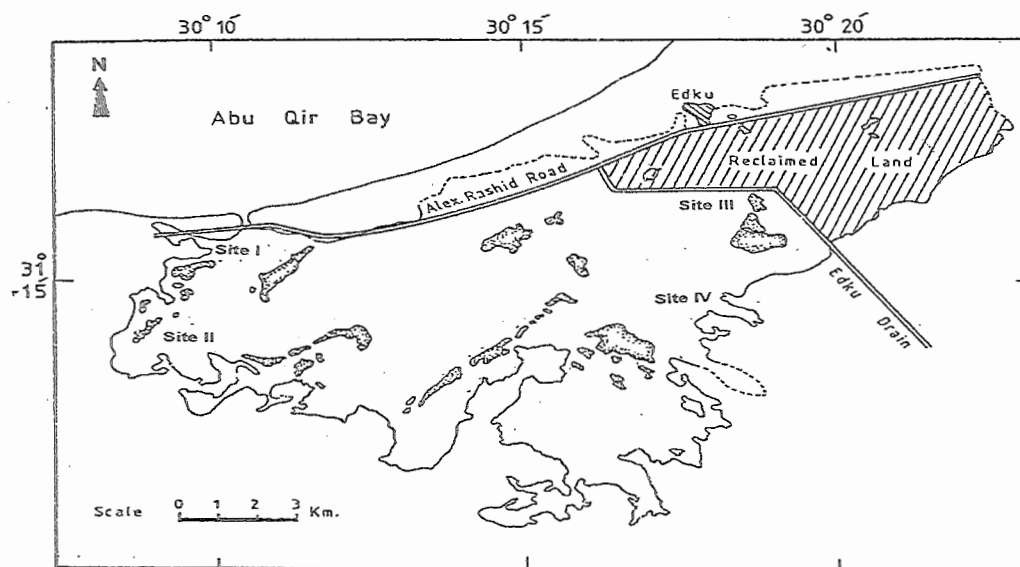


Fig. 1. Lake Edku and sampling sites.

The aim of this study was to determine of copper and manganese concentrations in surface sediments of Lake Edku and to identify their fractionation among different chemical forms by using sequential extraction techniques.

### MATERIAL AND METHODS

Surface sediment samples were collected by mean of plastic tube (PVC) inserted into the upper most layer of the sediments at four sites (Fig. 1) in Lake Edku. The wet sample from each station was divided into four subsamples, homogenized by mixing and put in clean plastic containers. All the samples were refrigerated immediately after collection, transferred from the field to the laboratory and stored deep frozen until analysis.

One subsample was used to determine chemical and physical characteristics such as grain size by wet sieving, water content at 105°C, and total organic matter. The calcium carbonate content was estimated using the calcimeter technique (Black, 1965). The total organic carbon (O.C.) was estimated as loss of weight percentage of the dried sediment sample after ignition (Dean, 1974). The percentage of organic matter was calculated by multiplying O.C x 1.724. The total concentration of Cu and Mn was determined using acid digestion with hot concentrated nitric acid mixed with 30% H<sub>2</sub>O<sub>2</sub>, 2:1 (Malo, 1977). Incomplete digestion of all sediment components was performed because trace metals bound to the internal structures of silicates were not needed for this type of study. Another wet subsample was subjected to sequential extraction technique. The extraction procedure was performed by using three replicate subsamples.

**Extraction procedure:**

For each subsample the sequential extraction techniques described by Tessier *et al.* (1979), Kersten and Förstner (1987) were applied (Table 1). In this procedure, the chemical extractants of the first steps were deoxygenated by bubbling nitrogen prior to contact with the samples. The tubes were closed with screw-caps during mechanical shaking and centrifugation procedures. A chelator (10 mg EDT A) was added to the ammonium and sodium acetate extracts to prevent precipitation of metals during storage in the refrigerator. Acidification of these solutions was found to be inadequate because of precipitation of humic acids leached by the first two steps (Kersten and Förstner, 1987). In the case of wet sediment samples, the concentration of each fraction was subsequently corrected for weight lost. Concentrations of different metals in the final extracts were measured using a Perkin-Elmer model 373 Atomic Absorption Spectrophotometer in the flame mode.

Table 1. Properties of the sediments used for sequential extraction technique.

Sample	Sediment type	Grain Size (%)			Organic Matter (%)	CaCO <sub>3</sub> (%)	Total elements (µg/g)	
		Sand	Silt	Clay			Mn	Cu
I	Sandy clay loam	58.94	17.4	23.66	3.06	9.6	355	42.3
II	Clay	13.30	30	56.70	8.11	4.1	275	53.8
III	Clay	37.16	20.77	42.07	7.19	4.4	564	49.5
IV	Silty clay loam	1.77	70.50	27.73	3.67	3.7	430	64.5

The extraction procedures for the different forms of the sediment samples were performed as follows:

**I- Exchangeable form:**

0.5 g sediment was weighed into a 50ml polypropylene centrifuge bottle and 8ml 1M NaOAC solution (pH= 8.2) was added. The contents were shaken for 2 hrs at room temperature and centrifuged; the supernatant was acidified and stored for analysis.

**II- Bound to carbonate:**

The residue from fraction I was leached at room temperature with 8 ml of 1 M NaOAC, adjusted to pH 5 with acetic acid; the contents were shaken for 5 hrs, centrifuged and stored the supernatant for analysis.

**III- Bound to easily reducible fraction:**

The residue from the step II was extracted with 20 ml of 0.1 M NH<sub>2</sub>OH. HCl in 25% (V/V) HOAC at 70°C (pH = 2). The contents were shaken for 6 hrs and centrifuged. The supernatant solution was collected and stored for analysis.

**IV- Bound to moderately reducible fraction:**

The residue from fraction III was extracted with 20 ml 0.2 M (N H<sub>4</sub>)C<sub>2</sub>O<sub>4</sub> and 0.2 M C<sub>2</sub>O<sub>4</sub>H<sub>2</sub> (pH = 3), shaken for 24 hrs and centrifuged. The supernatant was stored for analysis.

#### V- Bound to organic fraction:

The residue from fraction IV was extracted with 3 ml of 0.02M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> at 85°C (pH = 2). The contents were shaken for two hrs, after cooling, 5 ml of 3.2 M NH<sub>4</sub>OAC in 20% (V/V) HNO<sub>3</sub> was added and shaken for 30 min, and centrifuged. The supernatant was stored for analysis.

The accuracy of the method tested against standard reference material (IAEA-365, Monaco) ranged from 92.6 to 98% for Mn and 90.5 to 97.9% for Cu. In the present study, the precision of the extraction procedure was tested by using three replicate subsamples (air dry sample I) and subjected to the previous procedures. The standard deviations for the five tested fractions were 0.32, 0.86, 0.18, 0.47 and 0.15 for Cu and 0.11, 3.2, 0.84, 1.57 and 0.79 for Mn. The detection limits (µg/g) for the five fractions were 0.2, 0.7, 0.8, 0.8 and 1.2 for Cu and 3, 7, 5, 3, 4 for Mn.

The data revealed that coefficients of variation were 4.5% for Cu and 8.6% for Mn. Recovery of metal spikes added to the sediments with each batch of studied sediments were 92.5% for Mn and 94.8% for Cu. Sediment free blanks for metals were also prepared in triplicate, using the same standard procedure as that for the samples. Blank values were negligible for the metals under consideration.

## RESULTS AND DISCUSSION

The distribution of calcium carbonate content in the studied sediments is presented in Table 1. The maximum carbonate content reached 9.6% at St.I and the minimum value 3.7% at St.IV. Organic matter was fluctuated between 3.06% and 8.11%

The data as shown in Figure 2 and 3 showed the relative percentage of copper and manganese bound to the exchangeable form. These relative percentages from the total copper were 20.3%, 15.5%, 19.2% and 12.8% at stations I, II, III and IV, respectively, while the relative percentage of Mn content bound to the exchangeable fraction was 8.8% at station IV and ranged from 1.41% to 2.26% for the other stations. Comparing the present data with that reported of Lake Nasser (Shata *et al.*, 1993), the results revealed similar distribution in the content of Mn bound to the exchangeable fraction (4-8 %).

The amounts of both extracted elements bound to the exchangeable fraction (Table 2) indicated significant variations at the four stations. The mean value of the element content in this form ranged between 8.23±4.19 µg/g and 9.48±3.92 µg/g, for Cu and from 5.14±3.14 µg/g to 37.63±7.45 µg/g for Mn. It is clear from the results that the reducing conditions of the wet sediment affect the solubility of both manganese and copper to move towards the more easily extractable forms. These results agree with those found by Shuman (1980), who observed that the drying process before extraction decreased the extractability of iron, manganese and copper.

The results showed that the concentrations of the two reported elements bound to carbonate fraction were relatively high. The data, as shown in Figures 2 and 3 revealed that the relative percentage of their carbonate fraction ranged from 12.1 % at station II to 28.4% at station IV for Mn and from 17.4% at station IV to 27.7% at station III for Cu.

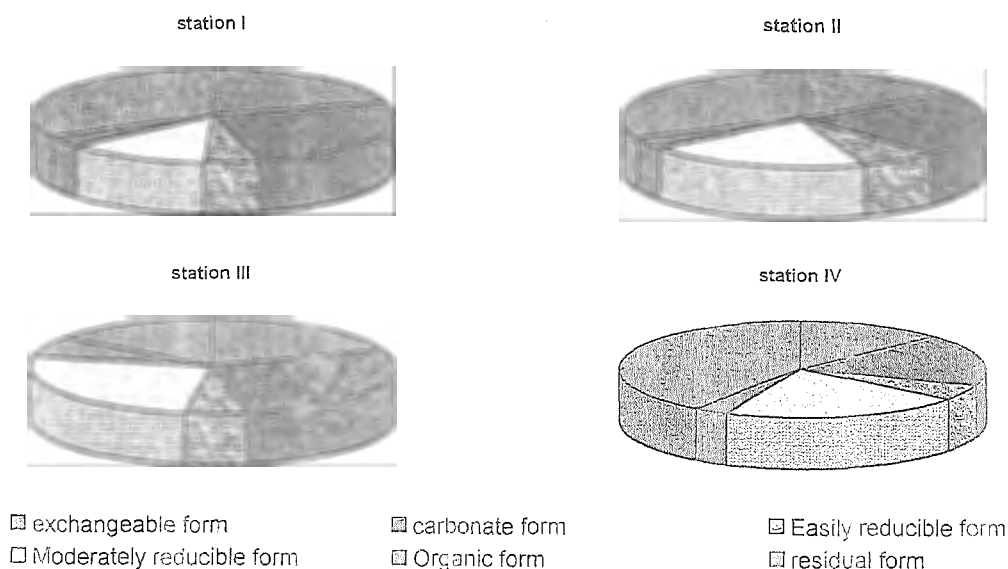


Fig. 2. The relative percentage of different chemical forms of copper in sediment samples for lake Edku.

The concentrations of copper bound to carbonate form revealed little variation among the four stations (Table 2). Its content ranged from  $10.79 \pm 4.17 \mu\text{g/g}$  to  $13.72 \pm 5.11 \mu\text{g/g}$ . A wide variation was noticed in the content of Mn associated with the carbonate fraction. It was  $84.47 \pm 1.81 \mu\text{g/g}$  for St. I,  $33.13 \pm 6.61 \mu\text{g/g}$  for St. II,  $118.27 \pm 21.36 \mu\text{g/g}$  for St. III and  $122.1 \pm 18.71 \mu\text{g/g}$  for St. IV. Compared with the other lakes, Shata *et al.* (1993) found that copper content as the carbonate fraction from Lake Nasser sediments was about 20.2% of the total element. In general, highest values of Cu and Mn contents associated with carbonate fraction may be due to the association of Mn with carbonate mineral phases such as calcite and dolomite (Okbah, 1995).

The results as shown in Figures 2 and 3 and Table 2 revealed that the values of copper and manganese contents changed to the easily and moderately reducible fractions. There was a trend towards increase of copper and manganese extractability at moderately reducible fraction in the four sediment stations. The differences of the values of copper and manganese content extracted in moderately reducible fraction reached from 2 to 7 folds more than that recorded in easily reducible fraction.

Table 2 shows that the amount of easily reducible fractions ranged from  $2.12 \pm 0.41 \mu\text{g/g}$  (St. I) to  $3.68 \pm 2.12 \mu\text{g/g}$  (St. II) for copper and between  $3.63 \pm 0.85 \mu\text{g/g}$  (St. III) and  $11.29 \pm 7.56 \mu\text{g/g}$  (St. IV) for manganese.

Figures 2 and 3 showed the variation in the content of copper and manganese associated with moderately reducible fractions and their relative percentage from the total element. The data showed that copper values increased from  $5.38 \pm 2.1 \mu\text{g/g}$  (12.72%) at St. I to  $13.73 \pm 1.12 \mu\text{g/g}$  (21.29%) at St. IV, while the content of manganese ranged between  $19.92 \pm 3.78 \mu\text{g/g}$  (7.24%) at St. II and  $33.42 \pm 6.67 \mu\text{g/g}$  (7.8%) at St. IV.

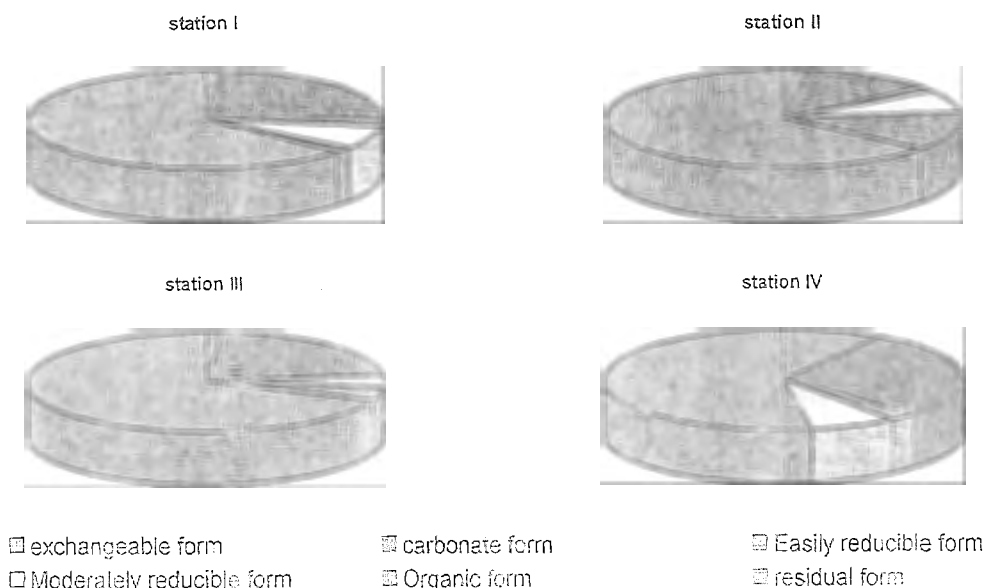


Fig. 3. The relative percentage of different chemical forms of manganese in sediment samples for Lake Edku.

In general, manganese can be presented as oxides, hydroxides or in association with iron oxides and hydroxides. Lion *et al.* (1982) showed that a high proportion of manganese is in the free oxide fraction, which would be solubilized with hydroxylamine hydrochloride. Also, it seems that manganese enrichment in the bottom sediments of Lake Edku precedes either through its adsorption onto the surface of the clay mineral. Compared with the sediments of Lake Borollos, manganese is present as both carbonate and residual fractions (Okbah, 1991). Shuman (1985) showed that copper was associated mainly with the Fe-Mn oxide fraction in sandy soil. The present data show that more than 60% and up to 85% in the fine fractions, while the remainder is found in the residual form. In contrast, most of manganese is recorded in the residual form, (more than 50% from the total).

The average of copper and manganese contents among the organic form is presented in Table 2 and the relative percentages from the total in Figures 2 and 3. The data show that copper mean values associated with the organic form ranged between  $1.67 \pm 0.75 \mu\text{g/g}$  at St. I and  $3.45 \pm 1.87 \mu\text{g/g}$  at St. III and its relative percentage ranged from 3.95% to 6.97%. Chester *et al.* (1988) recorded 50% of the total copper in the surface water particulate held in organic association and deposited at the sediment surface.

Organic copper is released subsequently as the organic carriers are destroyed. The organic -bound fraction of manganese ranges from  $5.91 \pm 2.72 \mu\text{g/g}$  (1.7%) at St. I to  $34.78 \pm 6.74 \mu\text{g/g}$  (12.65%) at St. II Shata *et al.* (1993) reported that manganese bound in three forms: oxide, organic, and residual.

**Table 2. Mean  $\pm$  SD, range for manganese and copper contains ( $\mu\text{g/g}$ ) in different forms of Lake Edku sediments.**

stations	Cu		Mn
	Exchangeable form		
I	8.57 $\pm$ 3.35		5.14 $\pm$ 3.14
	4.82 - 11.27		2.24 - 8.47
II	8.31 $\pm$ 3.09		6.22 $\pm$ 3.10
	6.19 - 11.86		3.84 - 9.73
III	9.48 $\pm$ 3.92		7.93 $\pm$ 4.43
	6.88 - 13.98		3.20 - 12.00
IV	8.23 $\pm$ 4.19		37.63 $\pm$ 7.45
	5.50 - 13.05		30.10 - 45.00
	Carbonate form		
I	10.79 $\pm$ 4.17		84.47 $\pm$ 1.81
	6.88 - 15.18		82.80 - 86.40
II	11.88 $\pm$ 6.00		33.13 $\pm$ 6.61
	5.80 - 17.80		26.48 - 39.70
III	13.72 $\pm$ 5.11		118.27 $\pm$ 21.36
	8.60 - 18.81		103.10 - 142.70
IV	11.21 $\pm$ 2.98		122.1 $\pm$ 18.71
	7.90 - 13.69		104.50 - 142.10
	Easily reducible form		
I	2.12 $\pm$ 0.41		7.97 $\pm$ 2.14
	1.72 - 2.53		6.40 - 10.40
II	3.68 $\pm$ 2.12		4.61 $\pm$ .93
	1.72 - 5.93		4.00 - 5.68
III	2.84 $\pm$ 0.50		3.63 $\pm$ 0.85
	2.43 - 3.39		2.80 - 4.50
IV	3.26 $\pm$ 0.39		11.29 $\pm$ 7.56
	2.97 - 3.70		2.67 - 14.4
	Moderately reducible form		
I	5.38 $\pm$ 2.10		26.52 $\pm$ 3.87
	3.40 - 7.59		22.35 - 30.00
II	10.75 $\pm$ 7.07		19.92 $\pm$ 3.78
	3.20 - 17.20		16.55 - 24.00
III	12.56 $\pm$ 3.53		22.38 $\pm$ 11.81
	8.60 - 15.38		8.75 - 29.60
IV	13.73 $\pm$ 1.12		33.42 $\pm$ 6.67
	12.60 - 14.83		26.67 - 40.00
	Organic form		
I	1.67 $\pm$ 0.75		5.91 $\pm$ 2.72
	1.16 - 2.53		3.76 - 8.96

*Table 2 Continued.....*

II	2.21 ± 0.67	34.78 ± 6.74
	1.72 - 2.97	27.59 - 40.96
III	3.45 ± 1.87	23.04 ± 6.30
	1.63 - 5.37	16.00 - 28.16
IV	2.06 ± 0.55	9.03 ± 6.04
	1.70 - 2.69	5.33 - 16.00

The results indicate that the distribution of copper among the different chemical forms of Lake Edku sediments obeys the following order: Cu-residual > Cu-carbonate > Cu-moderately > Cu-exchangeable > Cu-organic. The distribution of manganese among the six chemical phases of the lake follows the order: Mn-residual > Mn-carbonate > Mn-moderately reducible > Mn- organic > Mn- easily reducible > Mn- exchangeable.

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