

## COPPER CONCENTRATIONS AND PHASES IN POLLUTED SURFACE SEDIMENTS OF LAKE EDKU, EGYPT

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*Keywords: Lake Edku, sediments, Copper phases*

### ABSTRACT

The distribution of geochemical forms of a metal into the different sedimentary phases shows the important role of these forms in the cycling of metal between the water column and the sediment reservoir. The aim of the present work is to compare copper work concentrations among different phases at two periods. The evaluation was based on comparisons of the data of the different chemical forms extracted by using sequential extraction technique at two periods, 1992 and 2002. High copper content was observed in Lake Edku sediments, which originated from urban areas and industrial wastes as well as agriculture wastewater. Copper concentrations in the year 1992 in different species in the Lake sediments were considerably lower than that reported in the year 2002. Copper concentration in the different species reached 40 folds for exchangeable; 23 fold for carbonate 253 fold for Fe & Mn oxides; 2.6 fold for organic fraction and 33.8 fold for residual. The analysis of variance (ANOVA) for the two periods and sites showed significant differences in the content of copper during the two periods for the five fractions. The variance for the sites revealed no significant differences for exchangeable, carbonate and Fe & Mn oxides fractions.

### INTRODUCTION

Most of the trace metals become bound to particles in sediment, but a small quantity becomes dissolved in the water and can spread widely in the food chains. Sequential extraction is frequently applied for the fractionation of solid phase associated elements in sediments. These techniques are the key methods of investigating sediment contaminant. Partitioning Copper and other trace elements are potentially toxic at high concentrations, and may produce deficiency symptoms at very low concentration in the environment. The solid waste and wastewater usually contained considerable amounts of copper and other trace elements originating from industrial sources. In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals present in sediments, the types of association between metals and the sediment must be assessed.

Contaminants bind to different sediment phases (exchangeable, carbonate, iron oxides or organic matter) control their remobilization from the sediments. The knowledge of which forms a contaminant binds is vital for understanding contaminant fate within a water body. Several studies have been performed on trace element pollution in Lake Edku sediments (El Ghobary, 1977, Zazoo, 1977, Nessim, 1987, El Khatib *et al.*, 1994 and Okbah, 2002). Scientists have used sequential partial dissolution techniques to evaluate the more readily available forms of metals that are associated with sediments (Gupta & Chen, 1975; Tessier *et al.*, 1979). In spite of long analysis times, several studies have been carried out using this technique (Chapman *et al.*, 1998; Langston *et al.*, 1999 and Gümgüm & Oztürk, 2001). The aim of the present work is to compare copper concentrations among different phases at two

periods (1992 and 2002) using sequential extraction technique (Tessier *et al.*, 1979).

### MATERIALS AND METHODS

#### Study area:

Lake Edku lies in the north of the Nile delta, west of Rosetta branch between Long 30°8'30" & 30° 23' 00" E and Lat 31° 10' & 31° 18' N. It is one of four deltaic lakes that are connected to the Mediterranean Sea. The lake receives huge amounts of drainage water from three main drains (Fig.1), which open into the eastern basin of the lake. It is a shallow depth range between 0.25-5 m, Khadr, 1992), highly eutrophic lake. The sediments are enriched in nutrients from natural as well as anthropogenic sources.

#### Sampling and Extraction procedure:

Four samples were collected (during the periods of 1992 and 2002). From the surface sediment by means of plastic tube (PVC) trough digging gently into the upper layer of

the sediments. Sub sample was taken to determine chemical and physical characteristics such as grain size distribution by wet sieving, total organic matter (Dean, 1974) and CaCO<sub>3</sub> content was estimate using the calcimeter technique (Black, 1965). Total content of Cu was determined using acid digestion (Malo, 1977). For each Subsample the sequential extraction technique described by Tessier *et al.* (1979) was performed as shown in Table (1). Data were subjected to analysis of variance (ANOVA).

The accuracy of the method tested against standard references material (IAEA-365, Monaco) ranged from 90.5 to 97.9% using three replicate subsample and subjected to the procedures as described in Table (1). The standard deviations for the five tested fractions were 0.32, 0.86, 0.18, 0.47 and 0.15. The data revealed that a coefficient of variation was 4.5%. Recovery of metal spikes added to the sediments with each batch of sediments studied was 94.8%.

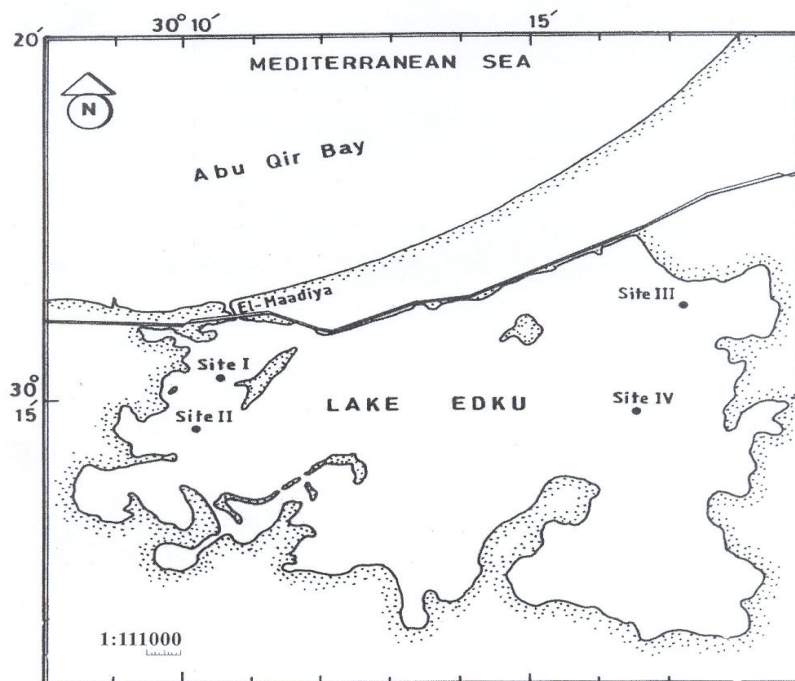


Fig.1. Lake Edku and sampling sites.

**Table (1):** The sequential extractions used to investigate Cu partitioning between five operationally defined fractions (Tessier *et al.*, 1979).

Step	Target form	Extraction conditions
I	Exchangeable	8ml NaOAC (1M) at room temperature, pH 8.2, shaking 2h.
II	Bound to carbonate	The residue from I+8ml Na OCA (1M) at room temperature, pH 5 (adjusted with acetic acid, shaking 5h.
III	Bound to Fe/Mn oxide	The residue from II+20ml NH <sub>2</sub> OH.HCl (0.1M) in HOAC 25% (v/v) at 70°C.pH2. shaking 6h.
IV	Bound to organic matter	The residue from III+3ml HNO <sub>3</sub> (0.02M)+5ml H <sub>2</sub> O <sub>2</sub> (30%) at 85°C and extracted with 5ml 3.2 NH <sub>4</sub> OAC (3.2M) in HNO <sub>3</sub> (20%), pH2, shaking 2h.
V	Bound to residual	The residue from IV was digested with mixture acid HF+HcIO <sub>4</sub> + HNO <sub>3</sub> (1:2:3).

## RESULTS AND DISCUSSION

Granulometric characteristics of the studied sediments and the total concentration of copper as well as organic matter and Ca CO<sub>3</sub> contents are shown in Table (2). The results revealed that the sediment type is characterized by relatively high content of clay. Total organic matter content ranged between 3.06% and 8.87%, while the carbonate content ranged between 3.7% and 17.3%.

Copper concentrations of the five fractions in the year 1992, (Table 3) ranged from 0.12 mg kg<sup>-1</sup> to 0.17 mg kg<sup>-1</sup> for exchangeable; from 0.32 mg kg<sup>-1</sup> to 0.60 mg kg<sup>-1</sup> for carbonate, from; 0.02 mg kg<sup>-1</sup> to 0.14 mg kg<sup>-1</sup> for Fe & Mn oxides; from 0.65 mg kg<sup>-1</sup> to 0.96 mg/kg for organic matter and residual fraction ranged from 0.80 mg kg<sup>-1</sup> to 1.41 mg kg<sup>-1</sup>. Comparing the results with that of 2002, the data revealed wide variation in the copper content associated with the five fractions (Table 3). The amount of copper extracted in exchangeable fraction (Table 3) indicates significant variations through the year 2002 comparing with those found in the year 1992, the content of Cu in the exchangeable form was increased to reach 40 folds in the year 2002 than that reported in the year 1992.

The analysis of variance for exchangeable-Cu contents showed significant differences for the two periods and no significant variation for sites (Fig.2). The results showed that the concentrations of copper bounded to carbonate and oxides are relatively high in the year 2002, ranged from 10.32 mg kg<sup>-1</sup> to 13.76 mg kg<sup>-1</sup> for carbonate and from 7.26 mg kg<sup>-1</sup> to 18.77 mg kg<sup>-1</sup> for Fe & Mn oxides correspondingly. These values increased than that observed in the year 1992, reaching up to 23 fold for carbonate fraction and 253 fold for oxides. Statistical analysis of variance (Fig.2) for Carbonate-Cu fraction and Fe & Mn oxides-Cu fraction revealed significant differences for the two periods and no significant difference were detected for sites (P<0.05). The study revealed that Cu is accumulated in the carbonate and oxides fractions as affected by the activity of mollusks shells and its precipitation within Fe & Mn Oxide and hydroxides. The data showed that copper content associated with organic form ranged between 0.65 – 0.96 mg kg<sup>-1</sup> 1992. These values increased 2.6 fold in the year 2002 found in the copper content bounded in the organic form which is ranged from 1.32 to 3.36 mg kg<sup>-1</sup>. The results of ANOVA test (Fig 2) showed significant differences for

both the two periods and sites for the organic and residual fractions.

The increase of copper content in the different forms in the two periods was resulted by many factors. Callender & Bowser (1980) reported that copper is mainly transported to the sediment in association with Biogenic carrier base. Chester *et al.* (1988) found that 50% of total copper in surface water particles is held in organic association. Collier & Edmond (1984) stated that released copper may be taken in other diagenetic phases such as oxides and carbonates. Cavallaro & McBride (1984)

concluded that microcrystalline and non-microcrystalline oxides in the clay fraction of the soil provide reactive surfaces for the chemisorption of copper. According to Harding & Brown (1975), copper is held in fine sediments in a variety of ways including metallic coatings, crystalline structure, organic matter and ion exchange sites. The Organic materials which are associated with silts and clays are also responsible for the increase of copper content in fine sediments as reported by Draz (1983).

**Table (2): Properties of the sediments**

Station		Sand	Silt	Clay	O.M. %	CuCO <sub>3</sub> %	Total Cu mg/kg
I	1992	9.15	63.5	27.35	3.63	8.69	2.67
	2002	58.94	17.4	23.66	3.06	9.6	42.3
II	1992	53.6	33.4	13.0	57.5	8.32	1.42
	2002	13.3	30.0	56.7	81.1	4.1	53.8
III	1992	27.8	50.1	22.1	6.35	17.3	1.78
	2002	37.2	20.7	42.1	7.19	4.4	94.5
IV	1992	35.7	53.3	11.0	8.87	8.63	2.11
	2002	14.2	64.5	21.3	3.67	3.7	64.5

**Table (3): Copper concentrations (mg/kg) in different fractions of Lake Edku sediments at two periods 1989 and 1998**

Station	Exchangeable		Carbonate		Fe & Mn oxide		Organic		Residual	
	1989	1998	1989	1998	1989	1998	1989	1998	1989	1998
I	0.17	4.82	0.32	10.32	0.14	7.26	0.65	1.32	1.41	18.58
II	0.12	6.88	0.56	12.04	0.02	17.79	0.73	1.93	0.00	15.16
III	0.14	6.88	0.54	13.76	0.04	18.77	0.80	3.36	0.27	6.73
IV	0.16	5.50	0.60	12.04	0.04	16.86	0.96	1.70	0.36	28.4
Mean	0.15	6.02	0.51	14.04	0.06	15.17	0.79	2.08	0.51	17.22
S.D.	0.02	0.89	0.11	1.51	0.05	4.62	0.14	0.77	0.54	7.76
Min.	0.12	4.82	0.32	10.32	0.02	7.26	0.65	1.32	0.00	6.73
Max.	0.17	6.88	0.60	13.76	0.14	18.77	0.96	3.36	1.41	28.4

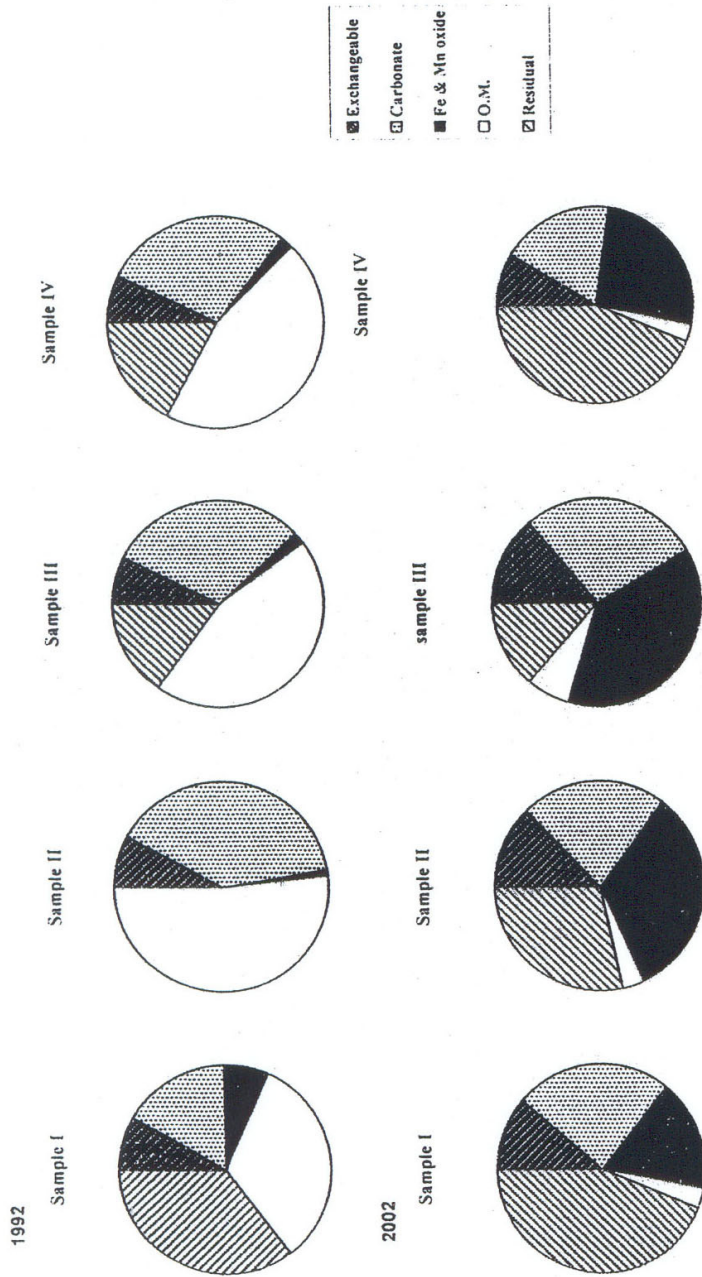


Fig. (2): The relative percent of copper forms in Lake Edku sediments at the two periods 1991 & 2002.

## CONCLUSION

Lake Edku sediment is subject to copper accumulation especially in the Fe and Mn oxides fraction rather than the organic, exchangeable, carbonate, and finally the residual fraction. The reason of such a distribution may be related to the organic carrier base, or the texture of the sediments itself or the metallic coating of the grains. It is clear from the results that sequential extraction technique is a powerful tool for understanding copper accumulation in sediments.

## ACKNOWLEDGMENT

I wish to express my deepest gratitude for Dr. Okbah, M. A. who provides the samples and help in preparing this manuscript.

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