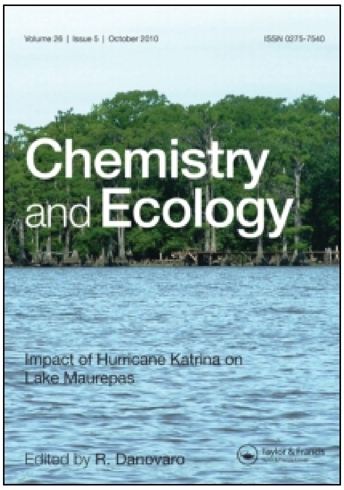

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FRACTIONATION OF Mn, Fe, Zn AND Cu IN SEDIMENTS OF KHOR KALABSHA, LAKE NASSER, EGYPT

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Khor Kalabsha is the second largest Khor in Lake Nasser, which is a freshwater side-branch of the main lake. Chemical analysis of the samples indicates that calcium carbonate and organic matter content in the surface sediments average 17.8 and 3.07%, respectively. Moreover, manganese, iron, zinc and copper concentrations are lower in Khor Kalabsha than in other lakes of Egypt. It has been found that both oxides and residual forms constitute the major part of the measured elements in the study area, while manganese and iron play an important role in building up clay minerals. It is noted that both zinc and copper fractions are controlled by biological and biochemical processes.

KEY WORDS Chemical fractionation, Khor Kalabsha, surface sediment, trace metals

INTRODUCTION

Sediments can be described as heterogeneous mixtures of organic and inorganic debris. Jenne and Luoma (1977) noted that any sediment matrix is likely to be associated with more labile and thermodynamically unstable components such as carbonate, amorphous aluminium silicates and organic matter. Most studies have dealt with total elemental concentrations. This can be accepted over geological time, but it is unsuitable for consideration of short term processes (Pohric, 1987).

Lake Nasser is considered the largest man-made lake in the world. It was formed after the construction of the Aswan High Dam in the southern part of Egypt. It lies between latitudes 23°58′ and 20°27′ N and longitudes 30°07′ and 33°15′ S.

Lake Nasser possesses numerous side branches called khors (Figure 1), which constitute about 76% of its total area. Khor Kalabsha and Khor El-Allaqi are the two largest Khors, having shorelines of about 700 km in length, which represent nearly 75% of the total length of all khors (Entz, 1974).

Khor Kalabsha lies on the western side of Lake Nasser, 55 km south of the Aswan High Dam. Khor Kalabsha is wide, flat, shallow and characterized mostly by a sandy loamy bottom. It extends for about 47 km westward with a shore length of 464 km, a mean width of about 13 km and a surface area of about 620 km^2 at 180 m above MSL (mean sea level). Khor Kalabsha is divided morphologically into three major parts; the main channel, northern and southern branches.

The aim of the present study is to determine the total concentrations of manganese, iron, zinc and copper in surface sediments of Khor Kalabsha and to identify their fractionation among different chemical phases.

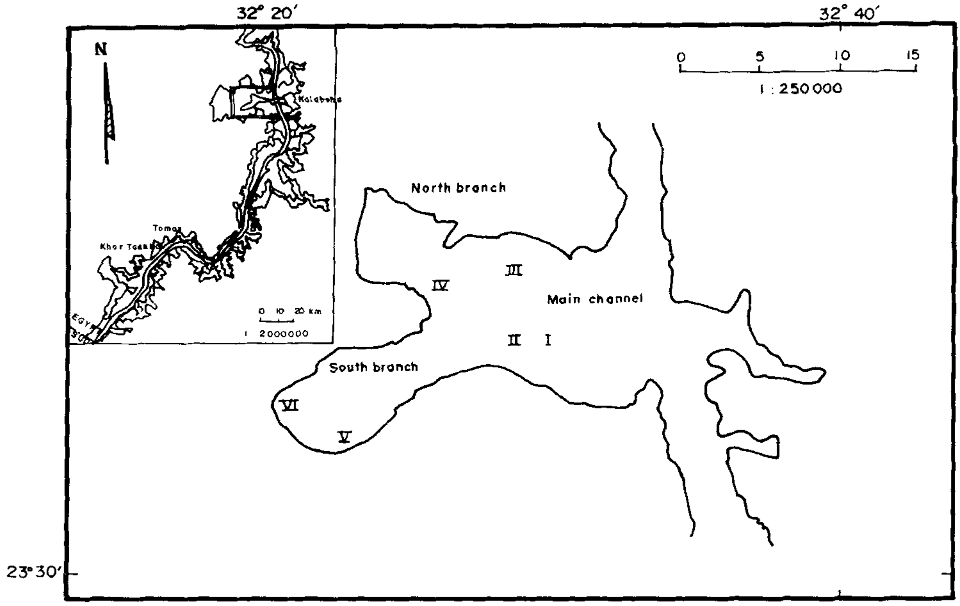

Figure 1 Location map of Khor Kalabsha, sampling sites I–IV.

Sampling and Methods of Analysis

Nineteen samples were collected from Khor Kalabsha in 1990. These samples covered the whole area, including south, north branches and the main channel. Sample sites I, II, III represent the main channel, site IV the north branch, and sites V and VI represent the south branch. The depth at which the samples were collected ranged from about 5 m to 28 m. The bottom samples were collected using a Petersen grab of 0.2 m^3 capacity. The depth of Lake Nasser in the main channel reaches to 75 m.

In the laboratory the samples were spread over glass sheets and left to dry in the air. The air-dried samples were disaggregated with the fingers and then split using the cone and quarter technique to ensure that representative samples were being examined.

The sample was divided into two portions. The first, unwashed, portion was subjected to sequential extractions performed according to Tessier *et al.* (1979) and Shuman (1985). The second portion was prepared for ordinary chemical analysis, whereas the air-dried samples were washed with distilled water. About 1 g of the washed samples was dried in an oven at 50°C, left to cool in a desiccator and then pulverized to pass through a 44-μm mesh sieve.

Analytical Procedures

Determination of organic carbon and total organic matter

Organic carbon was determined by the direct method described by El-Wakeel and Riley (1957). About 0.2 g of the dry sample was oxidized with 10 ml of chromic acid in a boiling tube (15 × 2.5 cm). The contents were warmed on a water bath for

15 min, cooled, and then about 200 ml of distilled water added. Titrimetric determination of the oxidant consumed was carried out against 0.2 N ferrous ammonium sulphate, using ferrous-phenanthroline as indicator. The percentage of total organic matter was obtained by multiplying the organic carbon percentage by 1.8 (Trask, 1939).

Determination of total carbonates

About 0.4 g of the dry samples was attacked by 2N hydrochloric acid in a calcimeter (Dietrich-Fruhling) and the volume of the evolved carbon dioxide measured (Black, 1965).

In order to follow up the distribution of manganese, iron, zinc and copper between different chemical phases, six samples were chosen to represent the whole of the studied area. The washed and dried samples were subjected to the following analyses:

1. Total elemental analysis carried out according to Oregioni and Aston (1984):
   A 0.5 g dried sample is digested with acid mixture ($HNO_3/HClO_4/HF$, 3:2:1) in a previously cleaned and dried Teflon beaker and evaporated to near dryness at 80°C. After complete digestion, 5 ml of 0.1M HCl at room temperature is added to rinse and transfer the residue to a 25 ml volumetric flask with extra HCl. Total manganese, iron, zinc and copper were measured by Perkin-Elmer 2380 AAS.
2. Sequential extractions which were performed according to Tessier *et al.* (1979), and Shuman (1985) as follows:
   a. The exchangeable fraction is extracted by 1M sodium acetate solution at pH 8.2 at room temperature for one hour with continuous agitation.
   b. The fraction bound to carbonate is extracted from residue (a) with sodium acetate solution at pH 5.0 for one hour at room temperature with continuous agitation.
   c. The fraction bound to iron-manganese oxides is extracted from residue (b) with 0.05 M hydroxylamine hydrochloride in 25% (v/v) acetic acid; this step is performed at 70°C with occasional agitation for six hours.
   d. The fraction bound to organic matter is obtained according to Gupta and Chen (1975).
   e. The residual fraction is computed as the difference between the total element concentration (from 1) and the sum of the other determined fractions (i.e. from a to d).

RESULTS AND DISCUSSION

The Nile sediments consist of terrigenous mud; their major fractions are silt and clay, while a minor part consists of fine and very fine sand. The mineral associations which characterize the Nile sediments are in the form of quartz, feldspar, epidote, monoclinic pyroxene, opaque minerals, micas and hornblende. (For more detals, refer to Emelyanov *et al.* 1978). Clay minerals are predominantly represented by the montmorillonite family (Venkatarthman *et al.* (1972).

The bottom sediments of Khor Kalabsha vary from very fine sand to sandy mud and sandy silt (Table 1), hence the sediments represent a favourable medium for adsorption processes. Mineralogically, the sediments are composed of clay minerals; quartz and feldspars are scarce (Saad and Shata, 1992). According to Elewa (1985) some silicate minerals, e.g. alkali-feldspar, can be completely dissolved by

Table 1 Chemical and physical properties of Khor Kalabsha sediments.

Station No.	Grain size distribution (%) Sand	Silt	Clay	Sediment type	Total organ. matter %	$CaCO_3$ %	Total concentration (ppm) Mn	Fe	Zn	Cu
I	12.60	56.63	30.77	Sandy mud	3.83	26.70	404.3	8716	250.6	119.6
II	33.62	53.14	13.34	Sandy silt	3.12	19.22	230.2	8192	148.5	158.1
III	87.46	10.48	2.06	Silty sand	1.53	11.34	100.7	5237	113.6	25.6
IV	73.33	20.09	6.58	Silty sand	1.04	12.36	177.4	7340	104.6	38.5
V	31.17	62.01	6.82	Sandy silt	2.81	17.46	273.1	8357	118.5	47.0
VI	19.32	52.30	28.38	Sandy mud	6.11	19.74	295.4	8803	114.5	30.0
Average	42.92	42.75	14.66	–	3.07	17.80	246.9	7774	141.7	69.8

Number of samples = 6; Number of analyses = 2.

weathering, also sodium and potassium are released in ionic solution. The chemical and physical analysis of the samples shown in Table 1 indicates that $CaCO_3$ content in the surficial sediments ranges from 11.3 and 26.7%, with a mean of 17.8%.

The origin of the carbonate in the area of study is mainly biogenic. According to Iskaros (1988), the freshwater gastropods recorded in Khor Kalabsha are represented by the species: *Bulinus truncatus, Physa acuta, Valvata nilotica* and *Melanoides tuberculata.* The shells of these organisms after death supply biogenic calcium carbonate to the bottom sediment.

The organic matter content of the sediments ranges from 1.04 to 6.11%, with a mean of 3.07%. Sediments of lower TOC content are confined to the northern branch where silty sand predominates, while the highest values are confined to the southern branch, where sandy mud predominates. The controlling factor for the organic matter distribution in the area of study is the texture of the sediments; according to El-Wakeel and Wahby (1970), it is influenced by water currents and related to the texture of sediments.

Metal Concentrations in the Bottom Sediments

Heavy metals reaching the lakes are derived by biological or physicochemical processes. Holmes *et al.* (1974) found that adsorption of dissolved zinc on to suspended sediment was achieved within one hour. This incorporation of trace elements into bottom sediments of Lake Nasser undoubtedly involves complex biochemical and chemical reactions between the water column, biota and sediments, as well as physical transport by water mass circulation. The distribution of total manganese, iron, zinc and copper in the surficial sediments of Lake Nasser is shown in Table 1. The average concentrations of these elements are 247, 7774, 142 and 70 ppm, respectively. Lake Nasser sediments have lower values than other lakes of Egypt and the world (Roy and Crawford, 1984; Pohric, 1987; Chester *et al.*, 1988; Moussa and El-Sayed, 1991). Table 1 shows that the total concentrations of the four elements are relatively lower at Station III (101, 5237, 114, and 26 ppm, for manganese, iron, zinc and copper, respectively) than at other stations. This could be explained as due to the difference in grain size. lower organic matter content and lower carbonate content of sediment at this station.

Metal Distribution in the Five Chemical Fractions

Manganese content

Manganese can be present 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. Figure 2 illustrates the distribution of manganese among the five chemical phases. This figure indicates that most of the manganese exists in two forms: oxides and residual, consisting of about 42 and 25% of the total.

Manganese content of the exchangeable fraction of the sediment of Khor Kalabsha is relatively low (4–8%) (Table 2). The organic-bound fraction of manganese ranges from 3.4 and 25.8%, with a mean of 8.8% of the total. Statistically, there is a significant correlation between manganese associated with the organic matter fraction and clay content (R=0.74) and also between the fraction present as oxides and bound to silt (R=0.83). Thus, manganese is distributed in three forms; oxides, organic and residual. It seems that manganese enrichment in the

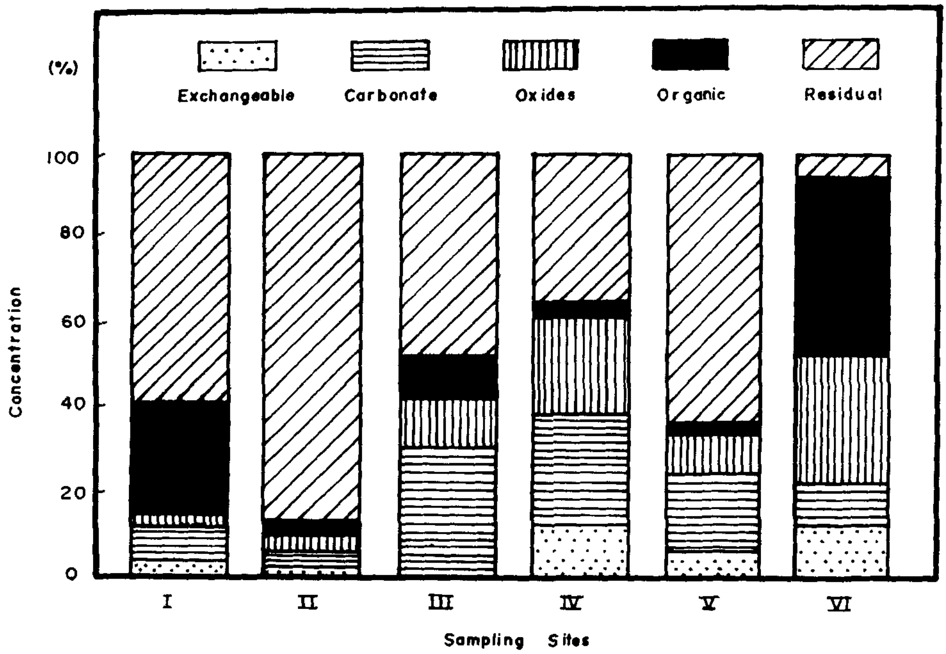

Figure 2 Percentage of manganese in sediment fractions.

bottom sediments proceeds either through its adsorption onto the surface of the prevailing clay mineral, i.e. illite (Saad and Shata, 1992), or through biological processes; Lake Nasser is highly productive, since it has an annual average standing crop of about 6.6 million units of phytoplankton per litre. The zooplankton population of the lake is also rich with an annual average of about 85,000 organisms m^{-3} (Zaghloul, 1985). Thus, a gradual sedimentation of organic material accumulates at the bottom through the annual introduction of flood water which enriches the lake with nutrients (Samaan, 1971). In contrast, in sediments of Lake Borollos (one of the cleanest lakes in northern Egypt), manganese is present as both carbonate and residual fractions (Okbah, 1991).

Generally, the distribution of manganese among the five chemical phases in the Khor Kalabsha obeys the following order of inequality:
Mn-oxides> Mn-residual> Mn-carbonates> Mn-exchangeable.

Iron content

Iron is considered as a conservative element, i.e. iron content in the exchangeable form is comparatively low and so the polluting effect of the iron in this area is negligible. Iron is principally associated with silt-clay fractions and is a mobile element; it is subjected to diagenetic remobilization (Forstner and Wittmann, 1979).

The distribution of iron among the five chemical fractions is presented in Table 3 and illustrated in Figure 3. High average values of oxides and residual fractions are obtained (29.3 and 65.2% of total iron, respectively) and are affected by oxic

Table 2 Fractionation of manganese in Khor Kalabsha Sediments (wet weight, ppm and fraction percent).

Station	*Exch.*		*Carb.*		*Oxide*		*Organ.*		*Resid.*		*Total*
No.	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*
I	25.19	6.23	63.05	15.60	154.49	38.21	104.46	25.84	57.10	14.12	404.30
II	9.35	4.06	28.82	12.52	111.42	48.40	11.88	5.19	68.73	29.86	230.20
III	8.08	8.02	21.70	21.56	25.85	25.70	3.47	3.44	41.56	41.29	100.66
IV	9.03	5.09	22.34	12.59	56.86	32.05	7.42	4.18	81.74	46.08	177.39
V	17.58	6.44	51.64	18.91	138.98	50.89	18.32	6.71	46.58	17.06	273.10
VI	26.03	8.47	67.96	23.01	169.42	57.36	22.28	7.54	10.69	3.62	295.38
Average	15.88	6.39	42.59	17.37	109.50	42.10	27.97	8.82	51.07	25.34	246.84

Number of samples = 6; Number of analyses = 2; ND = not detected.
Exch. = exchangeable; Carb. = carbonate; Organ. = organic; Resid. = residual

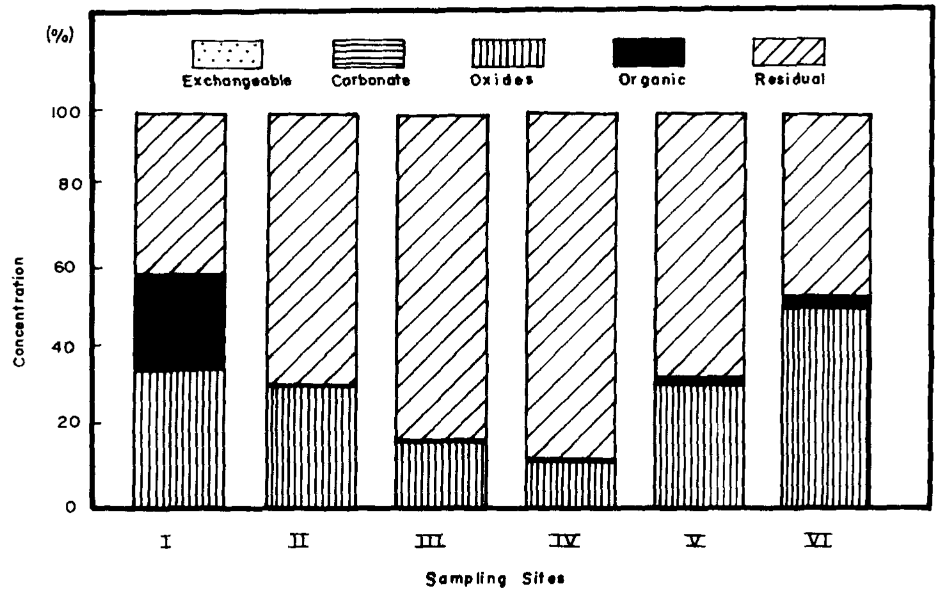

Figure 3 Percentages of iron in sediment fractions.

conditions. The iron associated with the organic fraction is statistically correlated with the clay fraction (R=0.7); also the iron oxide fraction is significantly correlated with the clay fraction (R=0.8) and silt (R=0.7), indicating that iron is either adsorbed or incorporated on to the surface of clay minerals. As described above, iron is distributed similarly to manganese, i.e. Fe-oxides and Fe-organic fractions are adsorbed on to the surface of the clay fraction, while the Fe-residual fraction is associated with crystalline Fe-oxides and clay fractions. So, the distribution of iron content in the five fractions obeys the following order of inequality:
Fe-residual> Fe-oxide> Fe-organic> Fe-carbonate> Fe-exchangeable.

Zinc content

The relative amounts of zinc among the different fractions of surficial sediments are shown in Table 4 and Figure 4. The most striking feature is the predominance of the oxide and residual fractions. Zinc in the oxide fraction has a range of 19.8–46.3%, mean 32.3%. The highest value (46.3%) is recorded in sediments of the southern branch of Khor Kalabsha which are characterized by high organic matter, a considerable amount of carbonate and sandy mud, favouring adsorption processes. Zinc in the carbonate fraction is highest in sediments of the southern branch (Station V, 32%), while the organic fraction also constitutes a considerable portion. Since the carbonate fraction is of biogenic origin, this reflects the considerable role of biological processes in the distribution of zinc fractions. In contrast to manganese and iron, Zn-oxide and Zn-organic fractions are weakly correlated with sand

Table 3 Fractionation of iron in Khor Kalabsha Sediments (wet weight, ppm and fraction percent).

Station	*Exch.*		*Carb.*		*Oxide*		*Organ.*		*Resid.*		*Total*
No.	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*
I	0.19	.002	14.70	0.17	3058.50	35.09	2078.50	23.85	3564.20	40.89	8716.1
II	3.16	0.04	14.70	0.18	2505.50	30.58	55.23	0.67	5714.30	68.53	8192.8
III	ND	ND	9.12	0.17	880.12	16.80	43.61	0.83	4304.50	82.20	5237.4
IV	3.16	0.04	18.79	0.26	866.62	11.81	78.49	1.07	6373.10	86.82	7340.1
V	0.19	.002	15.44	0.19	2593.14	31.03	142.44	1.70	5606.35	67.08	8356.6
VI	2.79	0.03	26.60	0.30	4468.00	50.75	281.98	3.20	4023.90	45.72	8803.3
Average	1.58	0.02	16.56	0.21	2395.30	29.34	446.70	5.22	4931.09	65.21	7774.4

ND = not detected.

Table 4 Fractionation of zinc in Khor Kalabsha Sediments (wet weight, ppm and fraction percent).

Station	Exch.		Carb.		Oxide		Organ.		Resid.		Total
No.	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
I	4.03	1.61	48.65	19.40	49.62	19.8	15.92	6.35	132 40	52.83	250.60
II	22.28	15.01	5.63	3.79	43.82	29.52	14.81	9.98	61.92	41.70	148.46
III	18.90	16.64	15.29	13.45	48.12	42.36	16.48	14.51	14.79	13.02	113.60
IV	16.95	16.20	13.87	13.26	31.58	30.18	27.59	14.64	14.00	104.63	
V	18.20	15.31	37.99	31.97	30.50	25.67	18.70	15.74	13.44	11.32	118.83
VI	6.60	5.75	13.21	11.54	53.06	46.34	17.59	15.36	24.07	21.02	114.51
Average	14.49	11.75	22.44	15.57	42.78	32.31	18.52	14.72	43.54	25.65	141.77

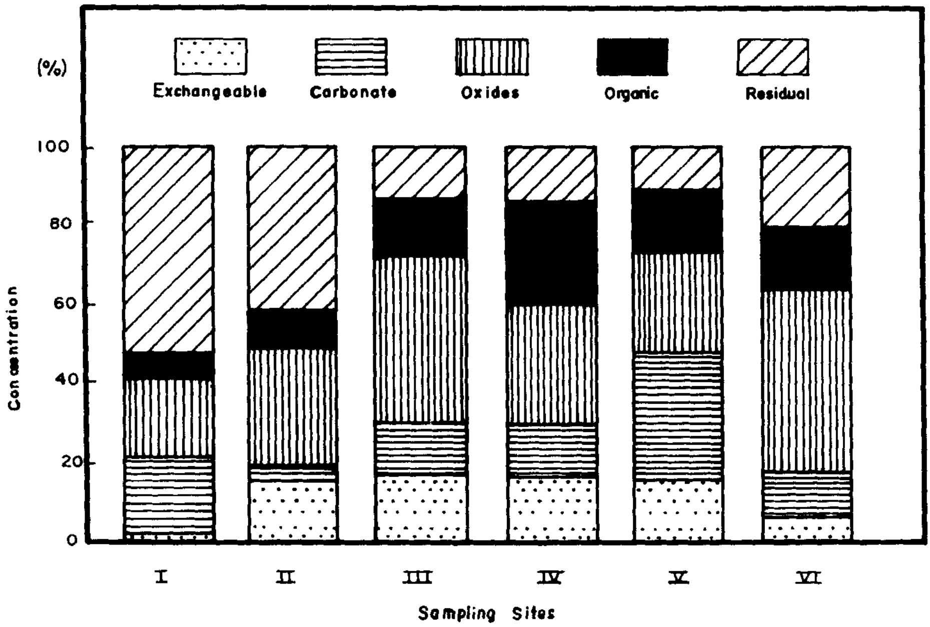

Figure 4 Percentages of zinc sediment fractions.

(R=0.35 and R=0.58, respectively). This reflects a very limited role of zinc in the formation of clay minerals in the area of study.

Generally, the distribution of zinc among the five chemical fractions in the bottom sediments of Khor Kalabsha follows the following order of inequality:
Zn-residual> Zn-carbonate> Zn-organic> Zn-exchangeable.

Copper content

The copper content of the surficial sediment fractions are given in Table 5 and the relative amounts of copper in different phases is highest in sediments of the main channel of Khor Kalabsha (26.8% of the total), associated with silt and clay (26.70%). Callendar and Bowser (1980) suggested that copper is mainly transported to the sediment surface in association with a biogenic carrier. Chester *et al.* (1988) reported that 50% of the total copper in the surface water particulates is held in organic association and deposited at the sediment surface. Organic copper is released subsequently as the organic carriers are destroyed.

Copper present as the carbonate fraction at all stations sampled averages about 20.2% of the total. The percentage of copper in the oxide fraction ranges from 2.5 to 23.2%. Shuman (1985) showed that copper is associated mainly with the Fe-Mn oxide fraction in sandy soil. Our results show that more than 50% of the total copper is concentrated in the residual fraction, while the remainder is distributed among the carbonate, organic and oxide fractions. Generally, copper distribution among the five chemical fractions obeys the following order of inequality:

Table 5 Fractionation of copper in Khor Kalabsha Sediments (wet weight, ppm and fraction percent).

Station	*Exch.*		*Carb.*		*Oxide*		*Organ.*		***Resid.***		***Total***
No.	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*	%	*ppm*
I	3.69	3.09	8.21	6.86	2.97	2.48	32.05	26.80	72.64	60.76	119.6
II	2.46	1.56	4.51	2.85	5.94	3.76	5.13	3.24	140.08	88.60	158.1
III	ND	ND	9.44	36.88	2.97	11.6	2.56	10.0	10.63	41.52	25.6
IV	4.92	12.79	11.49	29.87	8.92	23.19	1.28	3.33	11.85	30.81	38.5
V	2.87	6.11	6.97	14.83	4.46	9.49	1.28	2.72	31.42	66.85	47.0
VI	3.69	12.3	9.03	30.1	2.97	9.9	1.28	4.27	13.03	43.43	30.0
Average	2.94	5.98	8.28	20.23	4.71	10.07	9.19	8.39	27.85	55.33	69.8

ND = non detected

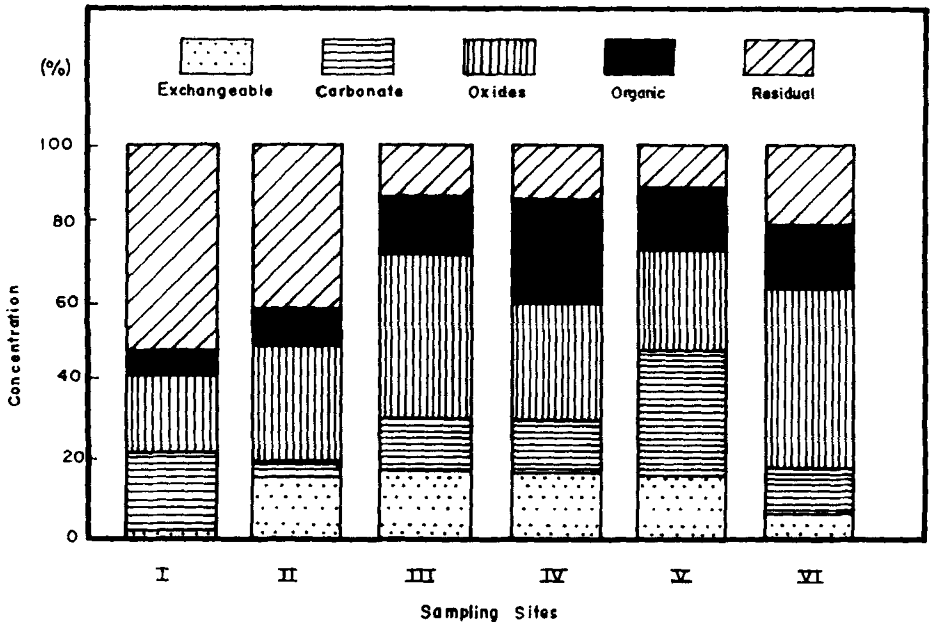

Figure 5 Percentages of copper in sediment fractions.

Cu-residual> Cu-carbonate> Cu-organic> Cu-oxide> Cu-exchangeable.

CONCLUSIONS

Khor Kalabsha is considered as a freshwater side-branch of the main lake, characterized by a carbonate content sufficient for certain species of molluscs. The high productivity in Khor Kalabsha indicates a significant role in the biologically mediated processes. The area of study is characterized by a relatively high organic matter content, which also influences the texture of the sediment. The area is covered mainly by coarse silt, considered as a depositional environment, hence it represents a favourable medium for adsorption processes. However, manganese, iron, zinc and copper concentrations are lower in the sediment of Khor Kalabsha than in sediments from other lakes in Egypt. The distribution of manganese and iron among the different chemical phases showed that most of the manganese and iron exists in oxides and residual fractions. The enrichment of manganese and iron in the bottom sediment of Khor Kalabsha proceeds through its adsorption on to the surface of the clay fraction, as well as through biological processes. The highest value of the zinc-oxide fraction is recorded in sediments of Khor Kalabsha, which are characterized by high organic matter, relatively low carbonate content and sandy mud. Generally, zinc and copper carbonate fractions are high in the sediment of the southern branch, where the zinc organic fraction constitutes a significant part. This reflects that in this part of the study area, biological processes play only a limited role in the distribution of copper and zinc. The comparison of the distribution of manganese, iron, zinc and copper among the different chemical phases reveals that:

1. The oxide-fraction constitutes the major part of the measured elements, reflecting their adsorption on to the surface of clay mineral.
2. The comparison of the order of distribution of these elements indicates that they are either supplied through mineralization or biological processes, i.e. either adsorption on the surface of the clay mineral or sedimentation of the organic debris.

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