TRACE ELEMENTS STATUS IN SURFICIAL SEDIMENTS OF LAKE MANZALAH, EGYPT

A. R. ABDEL - MOATI AND N. M. DOWIDAR

Oceanography Dept., Faculty of Science, Alexandria, Egypt.

ABSTRACT

The present paper includes detailed study on the geochemical status of nine elements (Al, Fe, Mn, Zn, Pb, Ni, Cu, Co and Cd) in the surficial sediments of Lake Manzalah, the largest northern Delta Lake in Egypt. Increased rate of drain water reaching the lake deemed it necessary to document and evaluate the important changes thast took place during the last 15 years. Attention was paid to the levels and distribution of both exchangeable and residual forms of these elements in lake sediments. The geaochemistry of these elements in the oxic and anoxic region of the lake was discussed. The relative abundance of studied elements was Al>Fe>>Mn>Zn>Pb = Ni>Cu>Co>>Cd. Intercomparison with other Nile Delta Lakes indicates the enrichment of Cu, Pb, Cd, and Co in Lake Manzalah sediments.

INTRODUCTION

Lake Manzalah is the largest of the four Nile delta lakes (about 60% of their total area). It provides more than 70% of the total inland fisheries of the country. Since the early 1920's the Lake received rather extensive work on the hydrography, water chemistry, flora, fauna as well as the biology and fisheries of its fish population. However, the Lake has received but few studies on the geochemistry of the Lake sediments since the end of 1960's. The size distribution of bottom sediments of the Lake together with the distribution of carbonate, organic carbon, organic matter, phosphorus and iron contents were studied by El-Wakeel & Wahby (1970). McComas (1983) reported on the levels and concentrations of some elements and pesticides in surficial sediments of the Lake collected in 1968.

In such a dynamic and in view of the increased role of drain water reaching the Lake, important changes have taken place which need to be evaluated and documented. For this reason the present work is deemed to be necessary. It includes detailed study on the status of nine elements in surficial bottom sediments. Attention was paid to the effect of fresh brackish and sewage water discharge on the levels and distribution of these elements in the Lake's sediments,

THE STUDY AREA

Lake Manzalah occupies the northern area between Damietta branch of the Nile and the Suez Canal (Long 31° 45'; 32° 15' E & Lat. 31° 00'; 31° 35' N) (Fig. 1). The Lake is connected to the Mediterranean Sea in the north through a narrow channel (Boughaz. El-Gamil) 6.5 m deep and 100m wide. permitting the continual exchange between lake and sea waters. However, the southern and southwestern borders are surrounded by cultivated lands. The present day area of the lake (according to land satellite Imagery, 1981), is 215,440 feddans(one feddan = 4200 m^2) of which 166,480 feddans (77.3%) are open water i.e. 700 Km^2 and 48,960 feddans (22.7%) are marshland and islands. The islands divide the Lake into well defined basins having more or less distinctive ecological conditions. The Lake is shallow with an average depth of about one meter. The total annual fresh and drain water inflow into the Lake is estimated at about 6680 x 10^{6}m^3. Of this water 78% is discharged by Hadus (agricultural drain, 49%), Bahr El Baqar (domestic and industrial seawge, anoxic, 25%), and Ramses (new reclaimed and agriculture lands, 4%) drains which open into the southern basin of the Lake (Fig. 1). The remainder 22% is agricultural drains and urban waste water.
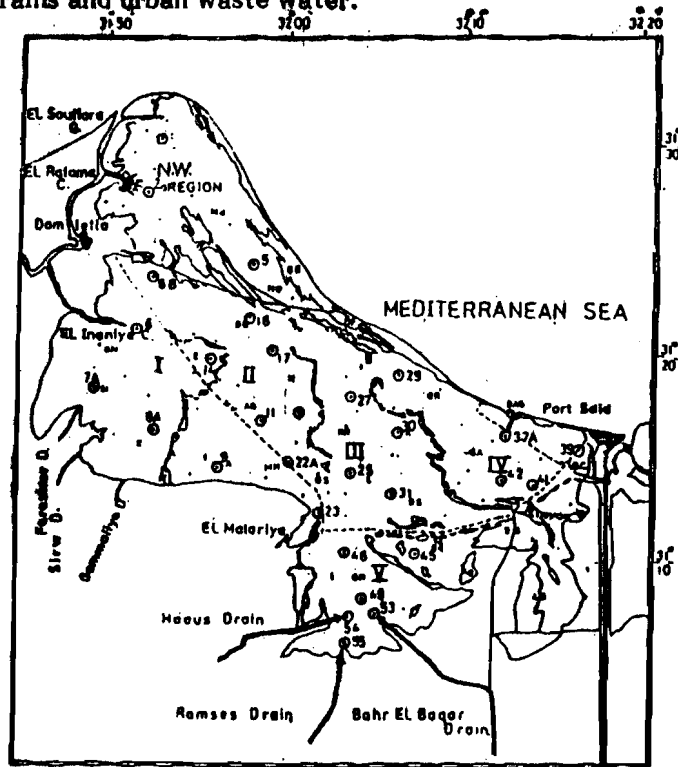

FIG. 1

Lake Manzalah, showing drains, canals, regions and zones I-V of the lake proper (stations sampled   ).

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MATRIALS AND METHODS

Using a modified Ekman grab, surficial bottom sediments were collected once, during March–April 1982 from 25 stations adequatelly covering the different lake's basins. Additional samples were collected from the mouths of differnt drains discharging into the Lake. This Samples were preserved freezed in self-sealed plastic bags.

Sediment samples were seived using an all plastic sieve where material > 2mm was discarded. Before commencing analysis, samples were dried using UNI-TRAP Model 10-100 freeze dryer. Exchangeable metals were extracted using 1M NaOAc (pH 8.2) for 1 hr as suggested by Gibbs (1973 & 1977). NH_4OAC (pH 7.0) extraction technique was not considered in the present study due to the possibility of attacking carbonates (Jackson, 1958 & Chapman, 1965). Chapman (1965) mentioned that the solubility of $CaCO_3$ is much lower in 1M sodium acetate at pH 8.2, a reagent currently used in measuring the cation exchange capacity of soils. The extraction time is likely to be sufficient for finely divided samples (Tessler et al., 1979). The pH of solution was checked periodically throughout the experiment. The solution was then filtered using Nucleopore filters (0.4 μ m porosity) where the filtrate was used for exchangeable metals determination.

Residual or total metals concentrations were determined using the method described by Hen drick (1968) using perchloric, hydrofluoric and nitric acid mixtures. Due to the high silicate content of Lake's sediment samples leading to highly turbid residues, the treating of samples with aqua-regia and allowing to stand under reflux in covered teflon beaker on hot plate for 2 hrs at 410° F before acid mixture treatment, was observed to give satisfactory results and kept from using Tessler's et al. technique (5:1 $HF/HClO_4$)(1979). Results of five replicate determinations of Standard Reference Material (SRM) No. 1645 River sediment from the National Bureau of standards tested for Zn & Fe using Tessler's technique (1979), Hendrick technique (1968) and modified Hendrick are shown in Table 1. It appeared that modified Hendrick technique gave the best results (low standard deviations) compared to those of the associated certificate even when tested for Pb, Ni & Cu.

The concentrations of Al, Fe, Mn, Zn, Cu, Cd, Pb, Co, and Ni were determined using Model 34000 Inductively Coupled Plasma (ICP)Emission Spectorometer provided with 48 channels, attached monochromator and computer controlled autosampler (Applied Research Laboratories). Concentrtation of exchangeable Zn (85% of samples), Pb and Cd were below the detection limit of instrument thus their results were not mentioned.

Figure 2 shows a comparison between the concentrations of copper and lead for Lake Manzala sediment samples measured by graphite furnace AAS (GFAAS) Model Hitachi 170-70 Zeemen effect, provided by an

TABLE 1
Mean replicate analysis for standard reference material for residual
metals using different techniques.

ELEMENT	Certified value standard reference material 1645 (NBS)	MEAN REPLICATE ANALYSIS		
		Tessier et.al.,(1979)	Nendrick (1968)	Present study
Zn (µg/g)	1720 + 169	1903.6 + 76.07	1660 + 140.12	1723 + 21.36
Fe (mg/g)	11.3 + 1.2	C.V. 4.045	C.V. 8.445	C.V. 1.245
Fe (mg/g)	11.3 + 1.2	12.824 + 0.997	10.736 + 0.364	11.69 + 0.231
		C.V. 7.775	C.V. 3.3 5	C.V. 1.965
Pb (µg/g)	714 + 28			715.8 + 22.98
				C.V. 3.215
Ni (µg/g)	45.8 + 2.9			45.9 + 1.12
				C.V. 2.435
Cu (µg/g)	109 + 19			103.04 + 5.4
				C.V. 5.225

autosampler and background corrector and the ICP emission spectrometer.
High correlations between concentrations reflect a good agreement between
results obtained from both instruments.

RESULTS

The areal distribution of residual and exchangeable forms of the nine
studied elements is represented in Figures (3 & 4). A common feature
of increasing levels of all residual elements was observed in the southeastern
basin of the Lake, an area highly affected by drain water discharge. For
most elements, values tend to decrease gradually towards the center of
the Lake. Patches of high concentrations were, scattered allover the lake
specially in the center of the western basin and near Port Said city sewage
out fall (Fig. 3). Generally, a quick sight to this figure shows that no regular
distribution could be observed for all elements. However, the western
part of the Lake and to a less extent the southwestern areas usually
represents the minimum range concentration of elements specially Al,
Zn, Ni and Co. Low concentrations of copper covers most of the central
and also the north-eastern region of the Lake.

The frequency distribution digram for all elements (Fig. 5) showed that
Al, Zn, Cu, Pb and Co are quiter egularly distributed between different
stations where most samples (50% or more) felt in the concentration range
40-50 mg/g, 60-80 µg/g, 20-40 µg/g and 20-30 µg/g, respectively. On
the contrary the concentration range of Fe, Mn, Ni and Cd occupied a
wider scale of variation reflecting high standard of irregularity and
patchiness.

However, apart from the smooth areal distribution of exchangeable
Co (Fig. 4b), the distribution of exchangeable Al, Fe, Cu, Mn, and Ni showed
a highly complicated picture. In case of cobalt, the Lake is nearly divided
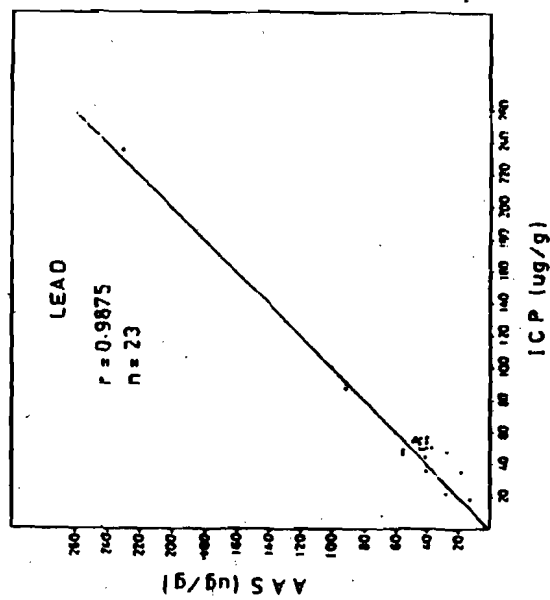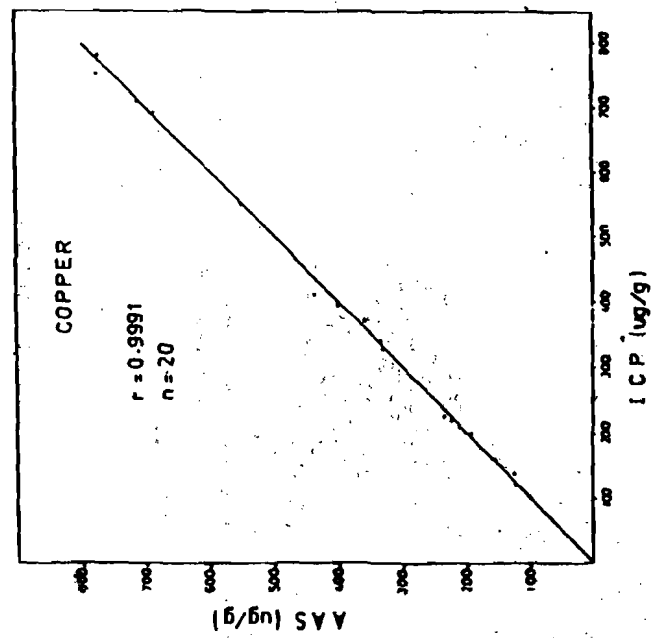
FIG. 2

Comparison between ICP and AAS analysis for copper
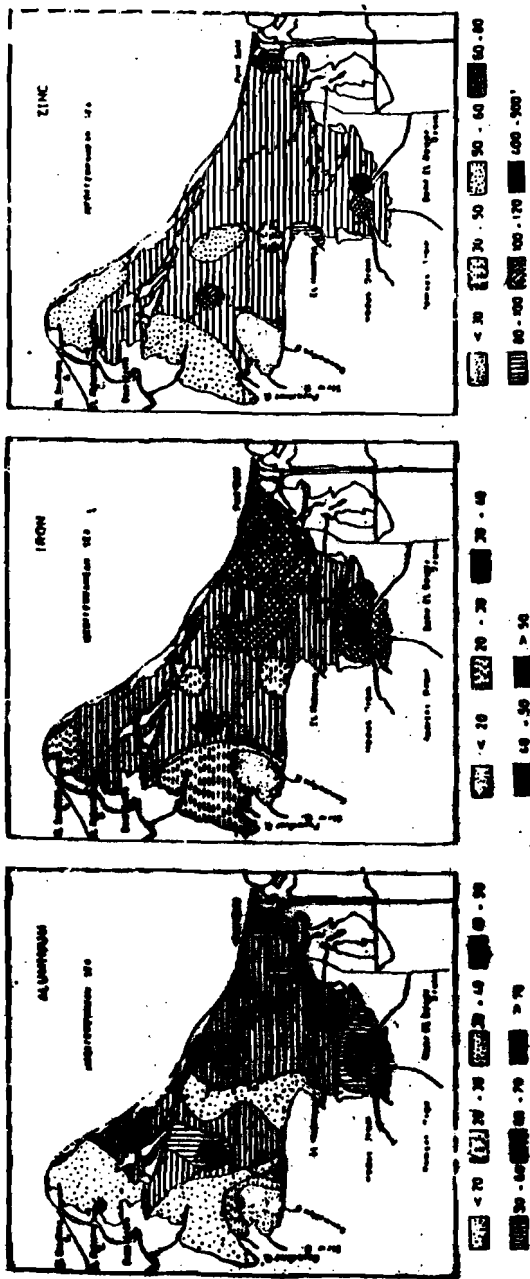and lead (µg/g) in lake sediments.

FIG. 3 (a)

Areal distribution of total Al, Fe & Zn in surficial
sediments of Lake Manzalah.

FIG. 3 (b)
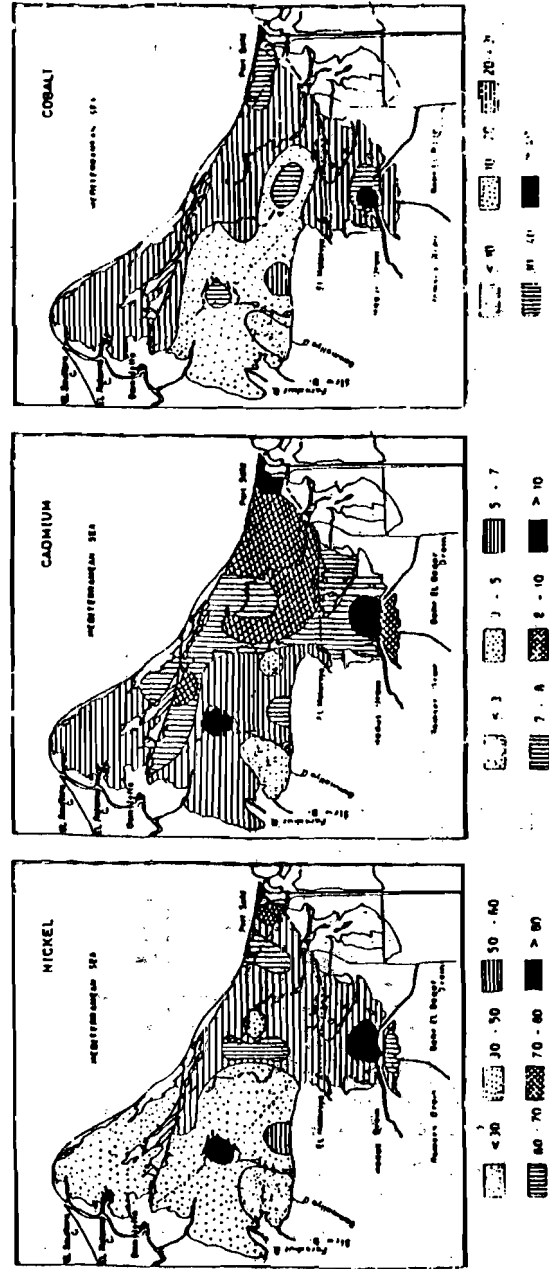Areal distribution of total Cu, Mn & pb in surficial sediments of Lake Manzalah.

FIG. 3 (c)

Areal distribution of total Ni, Cd & Co in surficial
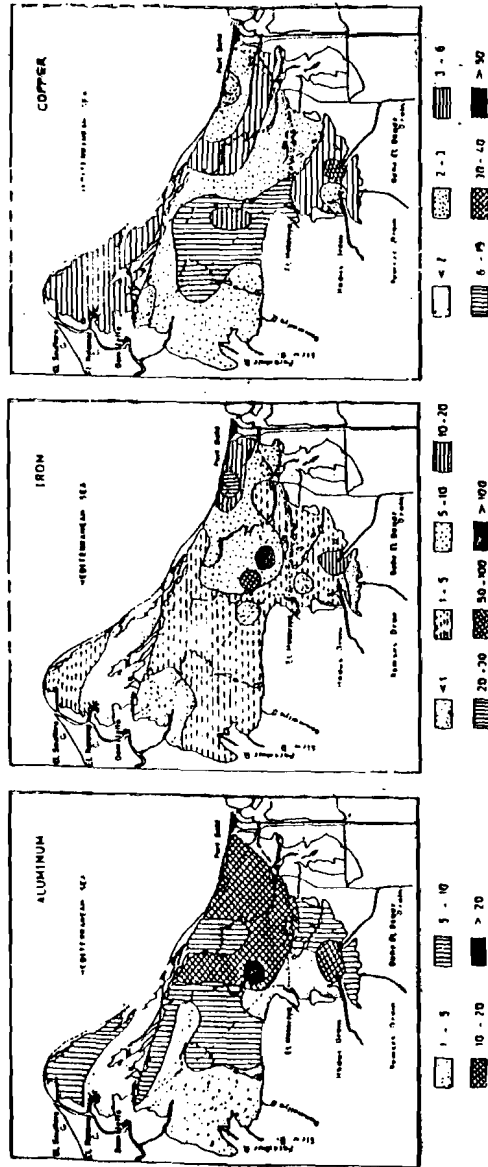sediments of Lake Manzalah.

FIG. 4 (a)
Areal distribution of adsorbed Al, Fe & Cu on surficial
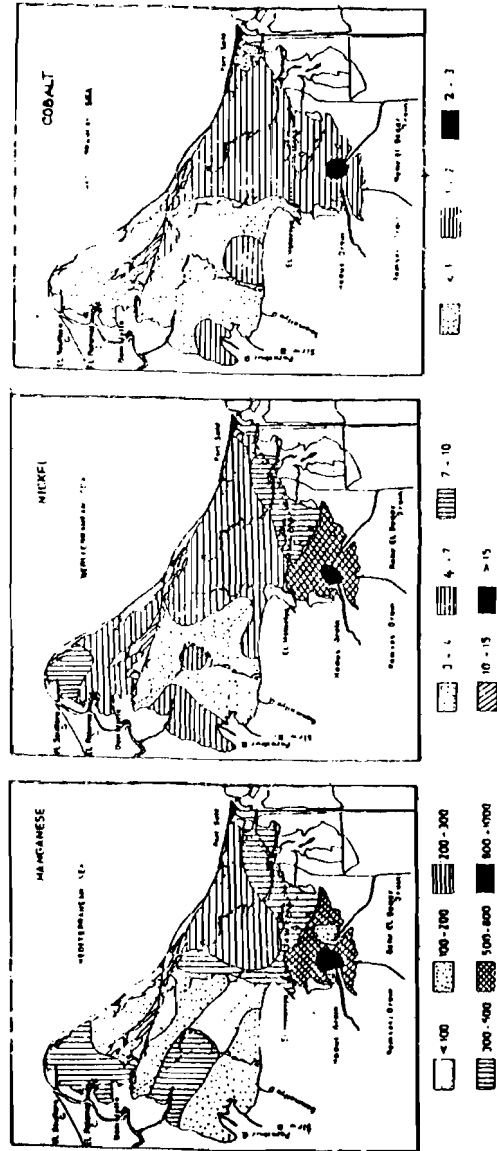sediments of Lake Manzalah.

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FIG. 4 (b)

Areal distribution of adsorbed Mn, Ni & Co on surficial
sediments of Lake Manzalah.
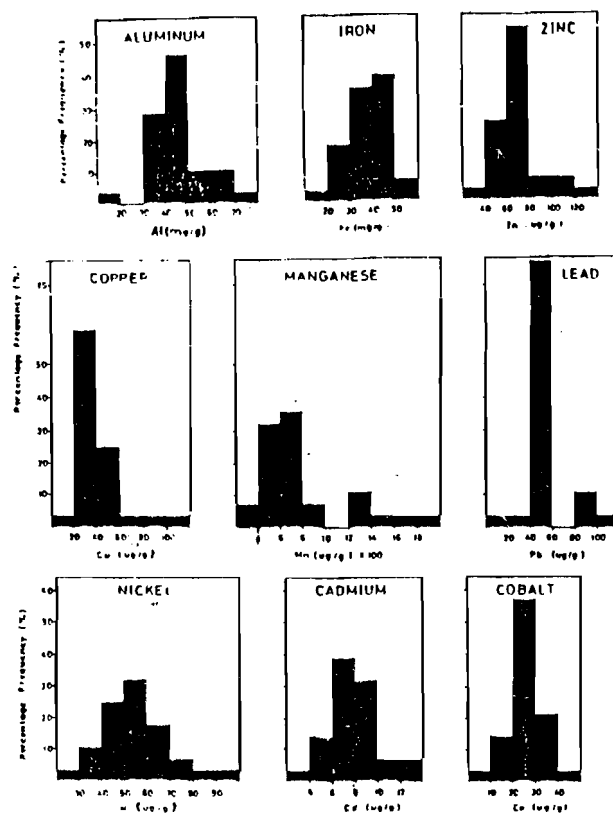
FIG. 5
Frequency distribution diagrams for total elements
determined in Lake Manzalah sediments.

into an eastern rich and western poor basins although patchs of high Co content (1-2 µg/g) were observed as spots in the southern zone of the western region (Fig. 4b).

The sediments off the mouth of Bahr El-Baqar drain are highly enriched with exchangeable cobalt (> 2 µg/g). In the case of Mn and Ni, the black spots indicating the high levels of both metals were observed also in the southeastern basin at the mouth of Hadus agricultural drain (Fig. 4b). The areal distribution of these two elements in the exchangeable form was in general nearly identical. High levels were observed in the southeastern basin with tendency of decreasing concentrations towards the

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central and northeastern areas. Maximum concentrations of Al, Fe and Cu were observed at the mouth of Bahr-el-Baqar and Hadus drains as well as the notheastern and central parts for Al (10-20 $\mu g/g$); patchy in the Lake center for Fe (50 - 7100 $\mu g/g$) and at Bahr-el-Baqar mouth for Cu (30-40 $\mu g/g$)(Fig. 4a). For sake of simplicity in data presentation the Lake is subdivided ecologically into 2 main regions; NW region (characterized by high salinity i.e.> 40% and Lake proper (salinity = 2.5%°) (Fig. 1). The Lake proper is also divided into 5 main zones. The average concentrations of the studied elements ($\mu g/g$) both in exchangeable and residual forms in each zone as well as drain water are given in Tables 2 & 3. Samples collected at the mouths of drains are not included in such average but treated seperatly.

TABLE 2
Average of total metal concentrations (µg/g) in surficial sediments of Lake Manzalah.

Region	Al	Fe	Zn	Cu	Mn	Pb	Ni	Cd	Co
N.W	30,533	32,267	59.3	47.9	717	64	47	6.3	22
	± 5,326	± 3,641	± 5	+11	+134	± 3,5	± 1.6	+1.1	± 1.7
Zone I	39,275	31,068	63.6	44.4	631	53.2	46.9	6.9	22.7
	±20,041	±13,210	±39	±34	±482	±30	±24	±3.5	±11
Zone II	39,444	32,736	56.4	54.6	508	47.8	44.6	6.5	22.3
	± 8,552	± 6,702	± 9.4	±31.6	± 80	± 8.5	± 8.3	±1.6	± 4.5
Zone III	45,477	39,026	71.5	37.9	755	51.2	55.5	7.98	27.9
	± 4,858	± 5,058	± 8.1	±14	±267	± 5	± 5.0	±1.1	± 5
Zone IV	49,738	42,740	72.7	35.6	696	54.8	60.3	8.8	29.8
	± 2,451	± 1,833	± 4.2	± 4.5	± 64	± 3	± 3.8	±0.4	± 3
Zone V	43,551	36,867	71.8	35.6	991	40.7	55.3	7.4	24 6
	±663	±419	± 7	± 1.5	±331	± 6.6	± 3	±0.04	± 1.6
B.Baqar dr	63,749	51,961	477.0	206	1799	166	82.6	12.1	38.1
Hadus dr.	75,173	50,968	107.2	63.6	1845	87.5	98.3	13.2	43.8

Zonal averages showed minute changes in between specially for residual elements. Zone IV (Northeast of the Lake) is characterized by elevated averages of most elements (Al, Pb, Ni, Cd and Co) while the bottom sediments of zones III and IV were enriched with Fe, Zn and Mn. Zone II which recorded the lowest average in nearly all elements recorded the highest average for copper i.e. 54.6 ± 31.6 $\mu g/g$ (Table 2).

The relative abundance of elements as observed from their average concentrations was:

TABLE 3
Average of adsorbed metals concentrations (µg/g) in
surficial sediments in Lake Manzalah.

Region		Al	Fe	Zn	Cu	Mn	Pb	Ni	Cd	Co
N.W.		5.4	0.72	B.L.	4.6	293	B.L.	6.4	B.L.	0.87
		±2.2	± 0.5	B.L.	±1.2	±118	B.L.	±1.6	B.L.	±0.1
Zone	1	5.03	2.7	B.L.	4.2	212	B.L.	4.9	B.L.	0.77
		±3.0	±1.9	B.L.	±3.3	±137	B.L.	±2.5	B.L.	±0.2
Zone	11	4.92	1.8	B.L.	5.73	147	B.L.	4.2	B.L.	0.82
		±2.5	± 1.2	B.L.	±5.1	± 52	B.L.	±0.8	B.L.	±0.19
Zone	111	12.3	32.8	B.L.	3.5	281	B.L.	6.5	B.L.	1.3
		±7	±46	B.L.	±2	± 89	B.L.	±1.2	B.L.	±0.3
Zone	IV	14.4	12.1	B.L.	2.8	294	B.L.	6.5	B.L.	1.15
		±1.5	±11.6	B.L.	±1	± 48	B.L.	±1.1	B.L.	±0.2
Zone	V	6.0	1.28	B.L.	3.2	445	B.L.	9.0	B.L.	1.2
		±4.7	± 1.2	B.L.	±0.3	±191	B.L.	±2.7	B.L.	±0.0
B.Baqar dr.		12.9	17.5	135	·33.7	163	B.L.	11.6	B.L.	2.2
Hadous dr.		12.4	4.02	0.96	2.3	960	B.L.	16.05	B.L.	1.5

* B.L. = Below detection limit of ICP-Es.

$$Al> Fe>> Mn> Zn> Pb = Ni> Cu> Co> Cd$$

in the residual (total) form. Regarding the order of abundance for the exchangeable fraction i.e.

$$Mn>> Fe> Al> Ni> Cu> Co$$

we can figure out that Mn and Al only have changed positions, with Mn as the most dominant metal in the exchangeable form. Interzonal variations are more pronounced in the case of exchangeable elements. Maximum averages for Fe and Co were observed in zone III, Cu in zone II, Mn and Ni in zone V and Al in zone IV (Table 3). Only the maximum of exchangeable Cu and Co recorded in zones II and III, respectively, coincided with their maximum residual forms in the same zones.

The average percentages of exchangeable / residual elements in the Lake sediments for each zone were calculated (Table 4) and found to be insignificant for Al (0.02%) and Fe (0.03%), low for Ni (12%),. Cu (9%) and Co (4%) but valuable for Mn where it reaches about 45% of the total manganese in the sediments of zone V of the Lake.

DISCUSSION

From the foregoing summary of results we can observe that the geochemistry of Lake Manzala sediments reflects to a great extent several conditions resulting from water inputs and different characteristics of

Region	Al	Fe	Cu	Mn	Ni	Co
N.W.	0.014	0.002⁻	9.6	40.9	13.6	3.96
Zone I	0.013	0.009	9.5+	33.6	10.4	3.39⁻
Zone II	0.012⁻	0.005	9.5⁺	28.8⁻	9.5⁻	3.96
Zone III	0.027	0.08⁺	9.2	37.2	11.7	4.66
Zone IV	0.029⁺	0.03	7.9⁻	42.2	10.8	3.86
Zone V	0.014	0.003⁻	9.0	44.9⁺	16.3⁺	4.88⁺
Mean(LP)	0.019	0.025	9.02	37.34	11.74	4.15
S.D.	±0.01	±0.03	±0.66	±6.5	±2.7	±0.6

N.B. Adsorbed fractions fro Zn, Pb, and Cd metals were below detection limit of ICP-ES
+,- indicate higher and lower values for each element.

bottom sediments. The predominant sediment is a complex type, sand-silt-clay, followed by clayey sand and silty clay, respectively. The boarders of the lake (affected by fresh and brackish water drains) are covered by silty clay. This material grades basin wards into sand-silty-clay which in turns encircles an area of clayey sand in the Lake center (El-Wakeel and Wahby, 1970). The sand fraction spreads along the north sides of the Lake derived from the Mediterranean beach sand. However, the distribution pattern clearly indicates a basinwards increase in grain size of sediments.

The distribution of trace elements in the Lake sediments is mostly controlled by the mineral composition of bottom deposits in addition to large amounts introduced into the Lake through agricultural, domestic or industrial wastes discharge. These additional sources cause some local increase in trace levels contents of areas affected by these inputs, In general, all total metals are enriched in the area affected by the two main drains, Hadous and Bahr El-Baqar (Fig. 3). At the mouth of Bahr El-Baqar drain the prevailing anaerobic conditons (Abd el-Moati, 1985) reduces the solubility of sulphate to hydrogen sulphide through biological activity of sulphate reducing bacteria. The H_2S produced reacts with available reactive metals and is fixed into botom sediments predominantly as sulphides. Because of the low solubility product of Zn and Cu sulphides, they are expected to be precipitated as sulphides duirng earlier diagensis. This probably explains the high Cu and Zn contents of the anoxic sediments of Bahr El-Baqar drain (Table 2). The concentrations of most trace elements in the sulphide bearing water of this drain is controlled by the solubility of the least soluble sulphid compounds.

Engler and Patrick (1975) observed that the stability of heavy metals sulphides (MnS, FeS, ZnS and CuS) in aerobic and anaerobic soils are directly related to their respective solubilities. They added that the order of reactivity is MnS > FeS > ZnS > Cus while the order of mobilization is roughly the inverse of that predicted from solubilities of simple sulphides.

Timperly and Allen (1974) mentioned that the accumulation of copper in reduced sediments, is mainly due to sulphide precipitation. This is reflected on the relatively low copper content of the overlying water (Abdel Moati, 1985) and enrichment in sediments. Fe and Mn are the elements that showed considerably high concentrations in tha anoxic water of Bahr El-Baqar drain. Lu and Chen (1977) stated that under reducing conditions Fe and Mn are released to interstatial water in significant quantities while the concentration of Cu, Ni, Pb and Zn are decreased mostly because of formation of solid sulphides. The high residual cobalt content of the sediments at the anoxic station is probably due to precipitation of cobalt and its incorporation into Lake sediments (Piper, 1971). In reduced soils and sediments containing sulphides, the precipitation of insoluble metal sulphides could be important in controlling the soluble levels of toxic metals (Hem, 1972; Holmes et al., 1974; Engler and Patrick, 1975; and Gambrell et al., 1976).

At the mouth of the agricultural Hadous drain with overlying oxic conditions, high values for residual iron and manganese were recorded in surficial sediments (Table 2). Under oxic conditions the solubility of Cd, Cu, Ni, Pb and Zn may increase due to formation of higher soluble solids while solubilities-of Fe and Mn might be decreased due to the formation of high oxidation states or lower solubilites oxides and hydroxides. According to Lu and Chen (1977) the formation of hydrated oxides of Fe and Mn occurred under two circumstances, viz: from sulphide oxidation to hydroxide or carbonate in surface sediments; and from the oxidation of the soluble species in interstatial water. Many soluble species in water could be scavenged due to formation of these oxides. This may explain the high cobalt content of the sediments in this area (Fig. 3c). El-Ghobary (1977) mentioned that high cobalt content or Lake Edku sediments is due to biogenic carbonate minerals and, to a lesser extent, to inorganic precipitation of association with caly minerals. Lu and Chen (1977) observed also the scavenging of other metals as Cd, Ni and Pb and attributed this to the formation of Fe and Mn oxides and the change in controlling the mechanisms from solubilities of sulphides to adsorption by other clay minerals. The removal of Ni by scavenging action of hydrous MnO_2 was demonstrated by Krauskopf (1956) who observed that clay minerals, apatite and organic matter are inffective scavengers.

The comparatively high aluminum content of sediments in front of both Hadous and Bahr El-Baqar drains reflects the abundance of this element as a major component of clay minerals specially at the mouth of Hadous drain where the clay content is about 63.6% (El-Wakeel and Wahby, 1970).

Away from the drainage area, natural forms and concentration of different metals began to appear. Solids of carbonates $CdCO_3$, Cu_2CO_3 $(OH)_2$, $NiCO_3$, $PbCO_3$, hydroxides $Fe(OH)_3$, Oxhydroxides [$FeO(OH)$, $MnO(OH)$], oxides (MnO_2, Fe_2O_3) or silicates ($ZnSiO_3$) probably dominate under aerobic conditions. Carroll (1958) stated that iron appears in the Lake sediments as an essential component of clay minerals, as minor constituent within their crystal lattice where it is isomorphous substitution as an iron oxide on the surface of mineral platelets.

On the other hand, Mn is mostly present in sediments in forms other than mineral form i.e. as precipitating coat on mineral species, organic matter and as iron-manganese hydroxide (Ilem, 1970; Gibbs, 1973 and Whitney, 1975). Both iron and manganese are known to be closely associated in the geochemical cycle (Krauskopf, 1967; Beltagy, 1973). This is clear from the positive correlation relating residual forms of both elements in Lake Manzala (r= 0.6747, p< 0.001). Phosphorous shows high affinity towards iron and to a lesser degree towards manganese (Berner, 1973). Based on unpublished data on the phosphorus content in the sedimetns of Lake Manzala, phosphorus is significantly correlated with Mn (r= 0.5156) while a poor correlation appeared with Fe (r= 0.1441). Laboratory experiments (El-Sayed, 1977) showed that manganese absorbs more phosphate ions than iron does. Beltagy et al.(1983) found a higher correlation between phosphorus and iron for sediments of the Nile delta and lower for manganese.

Significantly positive correlation between the metal composition of suspended matter and sediments (µg/g) were observed for Al, Fe, Mn, Cu, Pb and Co indicating the interaction between both phases . The concentrations (µg/g) of metals in suspenssion (Abdel-Moati, 1985) were higher than the corresponding concentration in sedimetns, except for Al and Fe. This indicates the role of TSM in enriching metals in sediments by precipitation of huge amounts of suspensoids carring metals to the bottom.

Comparing the results of the present study with those of samples collected from the Lake during 1968 (Table 5) elements could be classified to three

TABLE 5
Mean concentrations of studied elements in northern delta lakes compared with standard shale.

	Al (mg/g)	Fe (mg/g)	Zn (µg/g)	Cu (µg/g)	Mn (µg/g)	Pb (µg/g)	Ni (µg/g)	Cd (µg/g)	Co (µg/g)	Reference
L. Manzalah (NW)	35.5	32.3	59.3	47.9	717	54	47	6.3	22	Present work
L. Manzalah (LP)	44.2	37.0	89.1	49.7	720	57.4	53.8	7.7	26	Present work
L. Manzalah	22.4	44.5	119.8	207	766	9.6	63.1	0.17	-	(1)
L. Marlut	18.6	25.6	93.8	38	958	7.3	35.6	0.2	-	(1)
L. Burullus	-	4.5	-	0.122	0.68	-	-	-	-	(2)
L. Edku	-	8.5	-	298	1499	40	82	-	18	(3)
Standard shale	80	46.7	95	45	850	20	82	0.3	19	(4)

(1) McComas (1983)   (2) Darrag (1984)
(3) El-Ghobary (1977)   (4) Turekian and Wesepohl (1961)

groups, the first includes Fe, Zn, Cu and Ni where their concentrations have decreased with variable degrees. The second includes Mn which showed no significant change in concentration. The third group includes Al, Pb and Cd of which their values have remarkably increased. No records were mentioned for cobalt for 1968 samples. Increased water discharge of highly industrialized areas surrounding the Lake during the last 15 years may probably explain the elevated levels of Pb and Cd during the present study. Compared with other Nile Delta lakes (L. Mariut, L. Borollus and L. Edku), Lake Manzala is generally enriched in nearly all elements studied (Table 5).

Matching the average values of different elements with those of standard shale (Table 5) may give a quick practical means of tracing high elements enrichment which may be a source of environmental pollution or economically interesting mineral deposits (Turekian and Wedpohl, 1961). In comparison with standard shale results showed that Cu, Pb, Cd and Co are highly enriched in the sediments of Lake Manzala. Their source is mostly allochthonous as indicated by considerably low Fe/Cd and Fe/Co ratios of Hadous drain (3861 and 1164) and Fe/Cu and Fe/Pb ratios for Bhar El-baqar drain (252 and 313). The comparatively low Fe/Zn ratio at the mouth of Bahr El-Baqar drain (109)indicates that zinc is highly enriched in the anoxic station. Large volumes of waste water inputs may be an important factor in this enrichment. Forstner and Wittmann (1981) indicated that zinc enrichment is mainly associated with waste water effluents. The biogenic contribution of this element (also copper) is highly indicated. Copper is generally introduced to aquatic environments in two main forms lithogenic and/or biogenic (Draz, 1983); the former is essentially incorporated in clay minerals. Emelyanov et al. (1978) and Moussa (1977) stated that the terrestial part of copper is more pronounced. El-Ghobary (1977) mentioned that the Cu content of Lake Edku sediments is mostly biogenic in origin, it is concentrated in the different levels of the food chain and after decomposition of organic matter in sediment, free copper may be adsorbed on surface of clay minerals with different degrees. Forstner and Wittmann (1981) suggested that high copper concentrations may be a result of intermittent of the lakes with $CuSO_4$ to control algal growth. McComas (1983) stated that the source(s) of copper in Lake Manzalah has not been confirmed but one possibility is $CuSO_4$ applied both in the Lake and in irrigated fields as an algicide.

The variability of Lake Manzala sediments was reflected on its trace elements distribution. High positive correlation were observed between Al and all metals $P < 0.001$ (except Cu) indicating the association of these metals with clay minerals in the lattice structure. However, the poor correlation with copper i.e. $r = 0.1487$ indicates that a significant portion of copper may be of biogenic origin (El-Wakeel and Riley, 1961). The remarkably high positive correlation observed between Al and Fe i.e. $r = 0.9645$ indicates that ferric iron is associated with clay minerals or they form coating of iron oxides on the surface of clay or adsorbed on clay surface (El-Ghobary, 1977). Beltagy (1973) explained this by their probable association in the same mineral phase. Van Der et al. (1970) suggested that the bulk of Fe is present in clay minerals.

The increase in the levels of residual metals in the sediments of El-Gamil area (zone IV) is mostly due to coagulation of colloidal species to produce particulate forms in the mixed zone, some of which may be lost to the sediments (Sholkovitz, 1980).

Manganese in Lake Manzala was the highest exchangeable metal in the bottom sediments. Its percent to total manganese reached 45% in zone V. This indicates that the part of manganese bound to carbonates and organic content is relatively high. Adsorbed Cu and Ni also constituted considerable portion of the total concentration (about 10%).
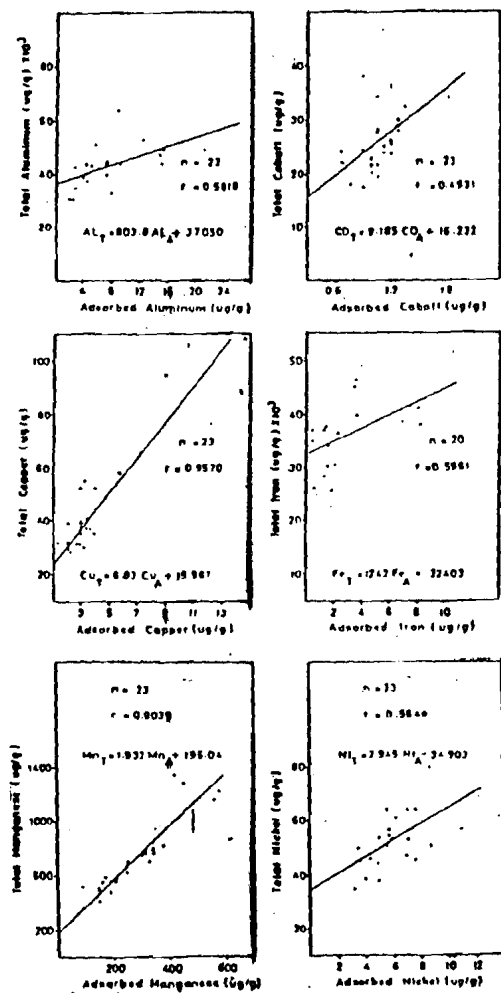
FIG. 6
Relationship between adsorbed and total trace elements
in surficial sediments of Lake Manzalah.

Variations in the adsorbed/total metals ratio of these two elements in the different zones were not significant (Table 4). The average percent of adsorbed iron and aluminum in zones II and IV were low following to a great extent their high total concentrations in both zones. Correlations between adsorbed and total forms of determined elements in Lake Manzala were statistically significant (Fig. 6) particularly for Cu and Mn (p = 0.001).

The remobilzation of metals from sediments is mainly controlled by the adsorbed processes. According to Forstner and Wittmann (1981), remobilization is mostly caused by four types of chemical changes in water : 1) elevated salt concentrations, 2) changes in the redox conditions, 3) lowering of pH, and 4) presence of natural complexing agents. In addition there are probably other biochemical processes by means of which metals adsorbed on surficial sediments are transferred to aquatic organisms to be further concentrated along the food chain or excreated directly as composition products into water.

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