

METAL DISTRIBUTION IN WATER AND SEDIMENTS OF LAKE EDKU, EGYPT

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ABSTRACT: Statistical methods are used to study the concentration variations for the heavy metals, Fe, Mn, Cu, Zn, Pb, Cd, Cr, Co and Ni at all stations in the different seasons. Higher values are recorded at the stations, which receive drain water. Organic matter, carbonate, phosphate, calcium, magnesium, and heavy metals were analyzed in sediment. The organic matter contents are of irregular trend affected by both agriculture and domestic effluents. The carbonate percent is increased in spring as a result of increasing photosynthesis. The phosphorous concentrations are affected by the sources of drain, agriculture effluents, phosphate fertilizers and organic matter precipitated in the surface sediment. Zinc and iron are of high concentrations in spring and autumn. Manganese concentrations show its maximum in spring and its minimum in winter. High content of copper is in summer and spring near drain. Cobalt is precipitated as cobalt carbonate as a result of Lake water alkalinity. The distribution of lead concentration is of irregular trend. The average cadmium concentration due to drain water is of high level. The high content of Cr was recorded in spring. The behavior of chromium and nickel was explained through their adsorption on iron and manganese oxides surfaces

Keywords: Metal Concentrations, Sediments, Lake Edku, Egypt

Lake Edku lies in the north of the Nile Delta, west of Rosetta Branch between longitude $30^{\circ} 8' 30''$ and $30^{\circ} 23' 00''$ E and latitude $31^{\circ} 11' 00''$ and $31^{\circ} 18' 00''$ N. It is a shallow brackish water basin with 17 km long. Its width is about 11 km at the widest part and about 5 km at the narrowest part. Its depth varies between 60 and 150 cm with an average of 1m. It is connected to the Mediterranean sea at the northwest end through a short channel called El-Boughaz (Khadr et al, 1992). The total area of the Lake decreased from 30,000 to 12,000 Feddans due to agricultural reclamation. Three main drains namely Edku, Bousily and Brezik discharge drain water to the Lake. Also it receives agricultural drain water at its eastern section where two main land drains discharge water through hydraulic pumps. The contribution of these land drains to the flow of drain water is ranging from 25.0 to 95.3 million m^3 per month. Lake Edku introduces an amount of 3.3×10^6 m^3 brackish water per day to Abu Qir bay through Boughaz El Maadiya. This work is disgned to detect the Lake Edku status especially the distribution of the metals in water and sediments so as to suggest recommendations for the improvement of its ecosystem. The obtained experimental data is analyzed using statistics

Material and methods

Surface water samples were collected seasonally from may 2001 to April 2002 at 20cm depth from ten different stations covering Lake Edku, Figure (1).

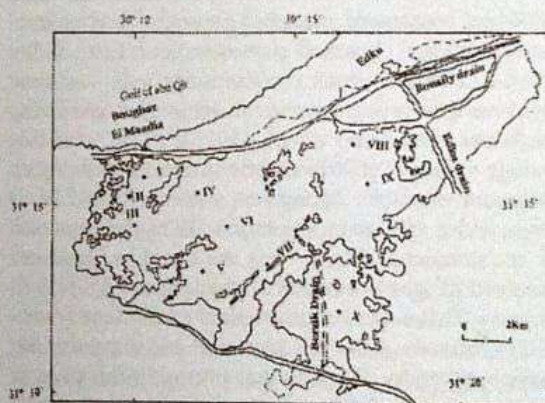


Figure 1: Map of the locations of sampling stations

Stations I and II are situated near El-Boughaz, which represents the area of Lake – sea connection. Station (III) lies to the west at Geziret El-Nagaa, which is affected by sea water enterance through El-Boughaz. Station (IV) is shallow with a depth range of 45-100 cm. Station (V) is located in south western part of the Lake, and is densely covered with Potamogeton *Pectinatus*. This area is sheltered and not affected by seawater. Station (VI) is located in the middle of the Lake. It is completely clean from macrophytes. It is affected by a permanent slow stream of water drain current flowing from the east to the west part. This may agitate in certain periods the bottom mud. Station (VII) is situated in south part of the Lake with the existence of macrophytes. Station (VIII) lies in the eastern side near the drains and is

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directly affected by drain water introduced through Edku and Bousily drains. Station (IX) lies to the east near Geziret El-Mayet. It is covered with the common macrophytes. This station is directly affected by drain water. Station (X) lies in Lake Ghitas, which is mainly affected by the Berzik drain. The samples were kept in well-stoppered polyethylene plastic bottles. The atomic absorption spectrometer is used to determine the metal concentrations according to standard methods. The sediment samples were collected using Ekman grab sampler, kept in polyethylene bags, washed with distilled water, dried at 85°C and then ground in an agate mortar. The organic matter % was determined according to (Allison et al, 1965) using oxidation behavior technique. The carbonate was determined by acid-base titration procedure (Jackson et al, 1958) and the total phosphorus was determined according to standard methods (American public Health Association (1975). Trace metals in sediment were expressed as ppm ($\mu\text{g/g}$) except for iron which it is expressed as (mg/g) due to its high concentrations in the sediments. The obtained data were analyzed statistically using the SPSS program.

Results and discussions

Table 1 shows the maximum and minimum values of seasonal, seasonal average and annual average of the chemical parameters of Lake Edku water. Most ferrous compounds in aquatic environments precipitate in alkaline and oxidizing conditions (Abdulla et al, 1973). The seasonal average values of dissolved iron concentrations has a maximum value of 1.21 mg/L at stations III and IX in spring and a minimum value of 0.03 mg/L at station VI in summer. This is due to the low level of dissolved oxygen at $\text{pH} > 7$ to precipitate $\text{Fe}(\text{OH})_3$ in summer. The negative correlation coefficient ($r = -0.307$) between dissolved iron and pH supports the above suggestion. The seasonal average values are in the order: spring, 0.67 > winter, 0.57 > autumn, 0.52 > summer, 0.19 mg/L. The higher values is due to high amount of the total suspended solids, TSS, that contain large amount of iron. The correlation between iron and suspended matter is positive ($r=0.326$). The low seasonal average iron content in summer is possibly due to the increased consumption of iron by phytoplankton in (Spencer et al, 1969). The removal of iron and other trace elements from the water system by planktonic organisms may take place through body adsorption and assimilation by organisms and subsequent transport as fecal material, (Brewer et al, 1975). The annual average value of iron is between 0.30 mg/L at station VIII and 0.82

mg/L at station I. The maximum value is due to iron used in building of International Coastal Road while the minimum value is due to the dilution of Lake water by agriculture and drain water sources. The high correlation ($r= 0.545$) between the concentrations of iron and manganese suggests that the association of the two elements originates from a common source during transportation and/or deposition reactions (Beltagy et al, 1983).

The minimum recorded value of Manganese is 18 $\mu\text{g/L}$ at station V in autumn and the maximum value is 112 $\mu\text{g/L}$ at station IV in winter. The seasonal average manganese concentration are in the order: autumn, 67.50 > winter, 62.31 > spring, 53.71 > summer, 47.18 $\mu\text{g/L}$. The high values were due to the increased consumption of this element by the phytoplankton in spring and (Emerson et al, 1993). The maximum annual average values of Mn, 75.25 $\mu\text{g/L}$ at station I is due to the higher concentration of the suspended matter and the minimum value, 28.83 $\mu\text{g/L}$ at station V in the middle of the Lake is due to the dilution effect for Lake water and the phytoplankton abundance. The maximum annual average Mn values at station I is accompanied by the maximum annual average of iron due to the precipitation of their hydroxides at the bottom. The high positive correlation ($r = 0.526$) between manganese and iron concentrations is probably due to their association as oxides and hydroxides (Degroot et al, 1975). The manganese toxicity is relatively low. The permissible manganese levels in water used for domestic purposes are <0.05 mg/L and the maximum acceptable concentration in water for continuous irrigation is 0.2 mg/l (U.S-EPA, 1972).

Zinc is one of the biologically significant known elements (Vinogradov et al, 1953). It exists in sea water in sub-micromolar concentrations (Vasanti et al, 1975). It has been reported that organic complexation controls the concentration of dissolved zinc in aquatic environment (Berg et al, 1987). Zinc is an essential for growth of marine organisms and its concentration affected by plankton communities (Hayward et al, 1969). The seasonal and regional values of the dissolved zinc concentration in Lake water is between a maximum of 126 $\mu\text{g/L}$ at station VII in autumn and a minimum of 11.0 $\mu\text{g/L}$ at station IV in summer. A maximum seasonal average value of zinc, 52.6 $\mu\text{g/L}$, was recorded in autumn while a minimum, 21.7 $\mu\text{g/L}$, was recorded in summer. The annual average values ranged between a maximum, of 57.55 $\mu\text{g/L}$, at station VII and a minimum of 8.85 $\mu\text{g/L}$, at station IX. Zinc was positively correlated with iron, manganese and copper ($r= 0.267, 0.290$ and 0.286), respectively.

Table 1: Maximum and minimum values of seasonal, seasonal average and annual average of the chemical parameters of Lake Edku water.

Parameters		Fe	Mn	Zn	Cu	Cd	Cr	Co	Pb	Ni
Values		mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Seasonal	Max.	1.21	18.00	126.00	49.00	16.00	26.00	23.00	225.00	110.00
	Min.	0.03	112.00	11.00	14.00	2.00	1.00	1.00	10.00	16.00
Seasonal average	Max.	0.67	67.50	52.60	32.10	8.50	11.10	10.70	89.40	40.90
	Min.	0.52	47.18	21.70	19.80	7.60	9.70	7.60	46.10	31.00
Annual average	Max.	0.82	75.25	57.55	31.50	11.75	16.50	14.00	95.50	51.50
	Min.	0.30	28.83	8.85	20.00	11.25	2.50	5.00	18.50	26.25

This correlation may points to the adsorption of zinc, manganese, and copper by hydrous iron oxides (El-Sayed et al, 1980).

The copper complexation in waters is affected by dense phytoplankton blooms (Hasle et al, 1981), and is strongly verified in spring. Copper speciation is influenced by biological and geological processes (Hasle et al, 1981). Its maximum values are between 49.0 µg/L at station VII in spring and 14.0 µg/L at station X in winter. The seasonal average copper concentrations are varied from 32.1 µg/L in spring to a lower value of 19.8 µg/L in summer. The lower values are due to the copper uptake by the living organisms. The maximum and minimum annual average copper concentrations are 31.50 and 20.0 µg/L recorded at stations VII and V, respectively. The values of 31.0 and 31.50 µg/L at stations V and VII are due to domestic sewage and drain water effect in the middle and east sectors of the Lake, where the domestic sources are the major contributors of copper in the environment (Kennicutt et al, 1982). The data indicated that the dissolved copper source in water is subjected to remobilization from sediments. However such approach extends to further steps, mainly adsorption and coprecipitation phenomenon of dissolved species onto suspended matter (Marshall et al, 1973).

Cadmium is extremely toxic to fish, (Green et al, 1986). Phytoplankton selectively play a significant role in scavenging of cadmium (Price et al, 1973). The maximum cadmium concentration is 16.0 µg/L at stations II and X in winter and summer, respectively and the minimum concentration is 2.0 µg/L at stations VIII and IX in winter and spring, respectively. The minimum values are due to the effect of Edku - Bousily and Berzik drains on the Lake water. The seasonal average cadmium concentrations, 8.5 µg/L in autumn and 7.6 µg/L in winter, are due to the rain fall dilution in winter (Duinker et al, 1974). The maximum value is due to high oxygen concentration with average (10.75 mg/l) which oxidize the cadmium (Duinker et al, 1974). The higher and lower annual average cadmium concentrations recorded are 11.75, 11.25 and 10.00 µg/L at stations X, II, and I, respectively and the minimum value of 4.0 µg/L is recorded at station VII

which is subjected directly to drain water. So the western part is more polluted than the middle part of the Lake while station X is subjected to agriculture

and insecticide drains which may cause raise in cadmium concentration.

Chromium is one of biochemically active transition metal in aquatic environment. Its concentrations gave minimum and maximum values between 1.0 and 26.0 µg/l recorded at stations VIII and II in summer, respectively. The seasonal average chromium concentration values are between 11.1 µg/l in winter and 9.7 µg/l in summer. The seasonal average value in autumn, 10.2 and in winter, 11.1 µg/l are higher than those in spring, 9.9 and in summer, 9.7 µg/l. This is due to the higher chromium consumption by phytoplankton in spring and summer, (Emerson et al, 1993). The maximum and minimum annual chromium concentration averages are 16.5 and 2.5 µg/l recorded at stations II and VIII, respectively. The higher value in western part is due to the seawater effect and many industrial wastes such as Abu Qir Fertilizer Company. The negative correlation between chromium and phosphate ($r = -0.372$) is a result of chromium phosphate precipitation (Marshall et al, 1973).

Cobalt is very important element in aquatic environment. Its moderat toxicity to most aquatic species is more than Cr³⁺ and Cr⁶⁺ but much less than Cd²⁺ and Cu²⁺. The present study indicated that the cobalt concentrations in Lake water are between a maximum value of 23.0 µg/L at station I in summer and a minimum value of 1.0 µg/L at stations IV and III in summer and autumn, respectively. The seasonal average cobalt concentration is between 7.6 µg/l in autumn and 10.70 µg/L in spring, which is due to cobalt contamination with phytoplankton that occurs in large quantity in spring season (Huzinger et al, 1980). The maximum and minimum annual cobalt average are 14 µg/L at station I and 5 µg/L at stations III and VIII, respectively. The annual average total dissolved cobalt values have a maximum amount at station I accompanied by a maximum annual iron and manganese averages suggesting the formation of hydroxides precipitates to the bottom or different complex structures with many organic ligands (Price et al, 1973). The cobalt toxic effects have been (Price et al, 1973).

Lead is very important in aquatic system. high concentrations of total Pb are often found in aquatic plants, particularly those growing in freshwater and receiving mine industrial wastes (Riley et al, 1958). The present results indicated that the maximum value

of 225 $\mu\text{g/L}$ is recorded at station III in spring, while the minimum of 10 $\mu\text{g/L}$ recorded at station II in spring and summer. The seasonal lead average is between 46.1 $\mu\text{g/L}$ in autumn and 89.4 $\mu\text{g/L}$ in spring. The datum is of typical anthropogenic and urban activities (Dekov et al, 1997). The annual average lead value is between 18.5 $\mu\text{g/L}$ at station II to 95.5 $\mu\text{g/L}$ at station VI. The higher Pb content in the middle part of the Lake is due to the effect of domestic drain water from Berzik and Edku-Bousily drains. The Pb concentration is affected by many small inflows, heavy rain and uptake by zoo- and phytoplankton (U.S- EPA, 1985).

Nickel results from industrial and urban activities (Dekov et al, 1997) and accumulate in many types of fishes and macrophytes. Its concentrations in Lake Edku water are ranged from minimum, 16.0 $\mu\text{g/L}$, at stations VIII in winter, to maximum, 110 $\mu\text{g/L}$, at station IV in winter. The seasonal average nickel concentrations are $40.9 > 36.9 > 32.4 > 31.0$ $\mu\text{g/L}$ for spring, summer, winter, and autumn, respectively. The high seasonal average nickel concentrations in summer and spring are due to nickel contamination with (Huzinger et al, 1980). The annual average nickel concentrations are between 26.25 $\mu\text{g/L}$ at station VI and 51.5 $\mu\text{g/L}$ at station IV. The lower value is due to nickel release from sediment at station VI in the eastern part of the Lake and the effect of drain water discharge. Total Ni residues may affect aquatic plants growth and fish (U.S- EPA, 1985).

The composition and structure of the sediment organic matter vary due to origin and geological history in the marine and aquatic environment. Phytoplankton and zooplankton are abundant sources of organic material in the sediments (Grathwohl et al, 1990) due to the contribution of terrigenous materials and plant and animal decomposition by the bacteria action (Draz et al, 1983). Table 2 shows the maximum and minimum values of seasonal, seasonal average and annual average of the chemical parameters of Lake Edku sediments. The organic matter concentrations are ranged from the highest value of 10.13 % at station III in summer to the lowest value of 3.26 % at station VI in winter. The seasonal average organic matter concentrations are between 5.85 % in summer and 5.02 % in autumn. The high organic matter value recorded in summer is due to large drain water amount. The extra - cellular products exudated by the hydrophytes and the precipitated planktonic organisms are expected to be the main autochthonous sources of organic matter in the Lake. The annual average organic matter contents are 4.66 % at station II and 6.09 % at station V. A major anthropogenic source for organic matter to the Lake is the Lake-Sea connection where cellulose remains derived from discharging from Racta and National paper Mills into Abu-Qir Bay. In general, the higher values of seasonal average organic matter

5.77, 5.85 %, recorded in spring and summer, respectively, are due to increase in chlorophyll-a content of the surface sediment during these seasons. Some factors control the quantitative distribution of organic matter content in the Lake sediments (El-Wakeel et al, 1970). The statistical correlations indicated that organic matter contents are highly correlated to some metals in the Lake sediments which is responsible for the ability of sediment to adsorb metals (Korickhaff et al, 1983). Positive correlation coefficient is recorded between organic matter and carbonate in Lake sediment ($r = 0.283$). This is mainly due to the fermentation process (Awad et al, 1993).

CaCO_3 precipitation is controlled by photosynthesis (Serruya et al, 1971). Although many calcite rich sediments may have large allogenic carbonate source, many other lacustrine carbonate sediments are endogenic. Their principal constituents have been precipitated directly from the water column (Lerman et al, 1978). The carbonate concentrations in Lake sediments are varied between 11.6 g/kg at station II in winter and 29 g/kg at stations VII in spring and summer. The seasonal average values of carbonate content in sediments are between 19.2 g/kg in winter and 26.3 g/kg in spring. The higher carbonate value is due to the aquatic plants and phytoplankton applied to extract CO_2 , and thus promote precipitation of carbonate at high pH (Lerman et al, 1978). The annual average carbonate concentration values are between 15.9 g/kg at station II and 24.4 g/kg at station IV. However, the value of 24.3 % is observed at station I near Boughaz El-Maadiya. The higher values are due to biogenic precipitation of organite by aquatic organisms building their calcareous shells (Aboul Naga, 2000). The sediments at station IV are rich in mollusca shells and partly of calcareous fragments (Latif et al, 1989). The relatively high values are due to the calcium rich water where CaCO_3 is precipitated at high pH during photosynthesis (Latif et al, 1989).

Both phosphorous and nitrogen are important elements controlling the growth and reproduction of phytoplankton (Ebeid et al, 1993). Phosphorous is necessary to all life due to its function in the cell energy storage and transfer and in genetic systems (Ebeid, 1993, Cole, 1979). The total phosphorous values in Lake Edku sediments are between a minimum of 0.03% at station VI in winter and a maximum of 0.71 % at station V in autumn. The latter is probably due to the decrease of decomposition of organic matter (El-Wakeel et al, 1970), and the drain water effect coming from Edku-Bousily and Berzik drains, agricultural drain and use of phosphate fertilizers. In general, the phosphorous supply in drainage water from the agricultural area is about 10 times greater than background (Hakansson et al, 1983).

Table 2. Maximum and minimum values of seasonal, seasonal average and annual average of the chemical parameters of Lake Edku sediments

Parameters Values		Fe g/kg	Mn mg/kg	Zn mg/kg	Cu mg/kg	Cd mg/kg	Cr mg/kg	Co mg/kg	Pb mg/kg	Ni mg/kg	O.M. %	CO ₃ ²⁻ g/kg	PO ₄ ³⁻ %
Seasonal	Max.	49.85	502.11	102.00	3.11	2.10	75.20	37.10	3.40	20.31	10.13	29.00	0.71
	Min.	16.90	113.00	17.00	0.80	0.22	30.00	5.10	0.89	11.10	3.26	11.60	0.03
Seasonal average	Max.	40.25	322.72	63.93	2.18	1.26	66.45	18.78	1.98	15.76	5.85	26.30	0.37
	Min.	27.47	264.18	59.30	2.10	0.89	45.35	13.83	1.58	14.04	5.02	19.20	0.16
Annual average	Max.	36.29	273.17	71.25	2.57	1.56	60.31	2.65	2.41	18.35	6.09	24.40	0.48
	Min.	27.40	226.35	52.00	1.83	0.62	45.83	9.73	1.15	13.79	4.66	15.90	0.22

The seasonal average value of phosphorous concentrations as phosphate ion are ranged in the order: 0.37 > 0.35 > 0.31 > 0.16 % for spring, autumn, summer, and winter, respectively. Such sequence is related to drain water and phosphorous dissolution from sediments to the overlying water as a result of resuspension of sediments by winds and boat movements. The annual average value of phosphorous concentrations 0.48, 0.33, 0.33% at stations V, IX, X, respectively are due to the use of inorganic fertilizers that washed down from the cultivated land to reach the Lake through the drainage system (Draz et al, 1983). An increase in the phosphorous content in sediments occurs through its release into solution by the bacteria action (El-Wakeel et al, 1970). The positive correlation coefficient ($r = 0.19$) obtained between the organic matter and phosphorous in the Lake indicated the discharge of the domestic sewage directly to the Lake (Draz et al, 1983). Phosphorous in the sediment is positively correlated with iron, manganese, zinc, copper, nickel, cadmium, cobalt and chromium, ($r = 0.625, 0.392, 0.422, 0.129, 0.497, 0.098, 0.107$ and 0.236), respectively. So, strong complexes formed between the metal ions and phosphate in the bottom water are adsorbed onto Fe and Mn oxides and hydroxides in the bottom sediments.

Some metals in potentially bioavailable forms can be transformed to the more readily available species by changes in the physico-chemical environment of the sediment - water system (Gambrell et al, 1976, Patric et al, 1977, Lee et al, 1975 and Leland et al, 1973). The total iron concentrations in the Lake sediments are between the minimum value of 16.9 g/kg at stations II and VI in winter and maximum value of 49.85 g/kg at station VIII in summer. The lower values of 16.9, 17.4 and 23.6 g/kg are recorded at stations, VI, VIII in winter and VII in autumn, respectively, and may attributed to resuspension of sediment with their adsorbed pollutants (Grobler et al, 1985). The seasonal average iron content in sediments are 40.25, 33.46, 33.36, and 27.47 g/kg for spring, autumn, summer and winter, respectively. The maximum value of Fe recorded during spring is due to a large amount of organic matter (5.77%), human activities accompanied with increase of the amount of domestic discharge from boats (Aston et al, 1973). Also, the high value recorded in autumn may attributed to high concentration of dissolved

oxygen, to facilitate the oxidation of iron from +2 to +3 accompanied with hydrolysis to precipitate the hydrous oxide on to the bottom sediments (Aston et al, 1973). The sediment acts as a major sink for pollutants in the aquatic environment where the suspended sediment particles settle the adsorbed pollutants to be removed from the water column (Aston et al, 1973). The annual average value of iron content in Lake sediment is between a minimum of 27.40 g/kg at station II and a maximum of 36.29 g/kg at station IX. The relatively high values of 36.29, 36.28, 35.09, 35.78 g/kg recorded at stations IX, VII, VIII, and I, respectively, are due to increase in clay content at these stations. The iron content is significantly correlated with manganese ($r = 0.418$). Both of the two elements are closely associated in a geo-chemical cycle (Beltagy, 1973). Also, the positive correlation is obtained between iron and zinc ($r = 0.561$) in Lake sediments may be attributed to sorptive properties of Fe/Mn oxides and hydroxides, where the oxygen donor groups (OH- or O-) on the surface of Fe/Mn hydroxides and oxides can react with metal cations in solution via complexing reaction (Stumm et al, 1976). A positive correlation coefficient ($r = 0.622$) is observed between iron and phosphate content in sediment. Phosphate ions adsorbed on the surface of these oxides can no longer stay at the adsorption sites (Williams et al, 1976). The positive correlation coefficient ($r = 0.302$) between iron and organic matter is related to the adsorption of iron on the complexing organic compounds, such as humic and fluvic acids (Luigi et al, 1991). The sediment ability to accumulate trace metals under oxygenated and anoxic conditions are evaluated using the distribution coefficient, K_d , term. The concentrations are in ppm units.

$$K_d = [\text{Metal}]_{\text{sediment}} / [\text{Metal}]_{\text{water}}$$

The maximum and the minimum K_d values of iron are 1.061×10^3 and 0.020×10^3 at stations, VI and I in summer, respectively. In general, the higher K_d , the stronger the sorption of the metal to the sediments (Salomons et al, 1980).

Manganese is found in minerals mostly as carbonates, oxides, silicates and sulphides. The manganese content in the Lake sediment is between a minimum of 113.00 mg/kg at station I in summer and a maximum of 502.11 mg/kg at station III in spring.

The variations in the manganese concentration in Lake sediment is probably due to the variation in the grain size of the sediments where the clay sediments are enriched in manganese (Draz et al, 1983). However, the seasonal average variations of Mn recorded showed that the values are between a minimum of 264.18 mg/kg in winter and a maximum of 322.72 mg/kg in spring. The latter is related to increasing amount of dissolved oxygen in water, which lead to oxidize manganese in water to solid MnO_2 precipitated to the bottom sediment. The annual average value of manganese concentration is between a minimum of 226.35 mg/kg at station II and a maximum of 373.17 mg/kg at station IV. This is attributed to the effect of increasing the organic matter at stations III and IV. On the whole, the high levels of manganese at stations III, IV and IX are attributed to muddy nature of the sediment at these locations (Darrag, 1984). Manganese is positively correlated with the organic matter in the Lake sediments, ($r = 0.297$) due to the high association of the metals with the organic content of the sediments probably bound to humic substances in water and sediments (Barsdate, 1970). Also, manganese in Lake sediments is associated with phosphorous where positive correlation coefficient ($r = 0.392$) is detected and is attributed to adsorption of phosphorous by Fe/Mn oxide in the sediment (Beltagy et al, 1983) as well as phosphate often present in domestic or industrial wastes. In addition, phosphate forms a strong complex with hydrated manganic hydroxide with formula $Mn_x(OH)_{4(x-y)}(PO_4)_y \cdot 2H_2O$ (Luigi et al, 1991). Based on Kd values for manganese, the highest value of 19.15×10^3 recorded at station III in summer indicated the high sorption of manganese in the middle of the Lake. The minimum Kd value of 1.17×10^3 recorded at station I in summer is due to the lower concentration of oxidized manganese in the sediment, where the amount of dissolved oxygen decreases in summer.

The zinc concentrations in Lake sediment are varied between 17 mg/kg at station V and 102 mg/kg at station I in spring. The maximum value is mainly due to the effect of seawater inflow through Boughaz El Maadiya affected by the industries and mining activities. The seasonal average variations of Zn are ranged between a minimum value of 59.3 mg/kg in summer and a maximum of 63.93 mg/kg in spring. The relatively high value may attributed to the high average seasonal metal content that precipitated at a high pH of 8.23 to be enriched with zinc and a high content of organic matter 5.77 % at the same season, where various metals are mainly bound to humic substances in water and sediments (Lasheen et al, 1981). The annual average values of zinc in the Lake sediments gave a maximum value of 71.25 mg/kg at station I and a minimum of 52 mg/kg at station VIII. In general, the Zn concentrations in the eastern and western areas of the Lake are higher than that of the median part, due to the effect of sea water entered to the Lake at west side and effect of drain water

entered to the Lake, in addition to industrial and agricultural activities along the eastern and northern parts of the Lake (Huzinger et al, 1980). The lowest annual average of 52 mg/kg at station VIII, is mainly due to the lowest Kd values of 0.672 to 2.34, i.e. low sorption of zinc in sediment (Salomons et al, 1980).

Positive correlation coefficients ($r = 0.422, 0.179$, and 0.551) are deduced between zinc with phosphorous, manganese and iron, respectively. These relations are attributed to adsorption of zinc by hydrous manganese and iron oxide. The magnitude of adsorption is increased with pH (Gadde et al, 1973). The distribution coefficient of zinc, Kd, is a maximum of 8.455×10^3 at station IV during summer and a minimum of 0.347 at station V during spring.

Copper is generally introduced to the Lake in two main forms, the lithogenic and biogenic (Salomons et al, 1980). Lithogenic copper is essentially found incorporated in clay minerals. It is known that after decomposition of organic matter the free copper may be adsorbed on the surface of clay minerals (Salomons et al, 1980). Copper concentration values are ranged from a minimum of 0.8 mg/kg at station III in summer to a maximum of 3.11 mg / kg at station I in spring. The seasonal average value of copper concentration ranged between 2.10 mg / kg in winter and 2.18 mg/kg in summer. The annual average variations of copper is fluctuated between 1.83 mg/kg at station X and 2.57 mg/kg at station I. The high value of Cu recorded at station I may be due to the effect of the seawater affected by industrial discharge from Fertilizers Company. While the higher values recorded at east direction of the Lake of 2.27, 2.32 and 2.36 mg/kg for stations VII, VIII and IX, respectively, are due to the effect of drain water discharged to the Lake. On the whole, there is no significant correlation coefficient between copper and most components of the sediment. However, only positive correlation with phosphate is observed of ($r = 0.184$), Fe (0.161), Zn (0.145), carbonate (0.422) and Ni (0.153). The data indicated that association of metals with clay minerals or the adsorption of copper on iron oxides occurred in addition to precipitation of copper. The positive correlation between copper and phosphate is due to the existence of charged clay particles responsible for sorption of both cations and anions (Grobler, 1985). The distribution coefficient, Kd, of copper shows a minimum of 0.047×10^3 at station VII in autumn, and a maximum of 0.178×10^3 at station VII in summer. The higher Kd values indicated stronger sorption of copper to the sediment where Cu is strongly adsorbed to the surface of manganese oxide.

In the present study cobalt concentrations are between a minimum of 5.1 mg/kg at station IX in summer and a maximum of 37.1 mg/kg at a station IV in spring. The seasonal average value of cobalt is ranged in the order: $18.78 > 14.32 > 14.28 > 13.83$ mg/kg for the Lake sediments during, summer, winter and autumn, respectively. The variation of the

concentration of cobalt depends on the structure of sediment and clay. For annual average studies, the maximum value of 20.65 mg / kg is given at station IV, while the minimum at station X is 9.73 mg/kg. Cobalt is positively correlated with carbonate ($r = 0.248$) and with pH ($r = 0.140$), both are related to precipitation of cobalt as $\text{Co}(\text{OH})_2$ and CoCO_3 . The positive correlation between cobalt and phosphate ($r = 0.107$) in Lake sediments, is due to the existence of charged clay particles and anions (Grobler, 1985). However, the correlations between Co and Fe, Mn, Zn are (0.288, 0.330, and 0.226), respectively indicated the association of the metals with clay minerals or the adsorption of both Co and Zn on the Fe_2O_3 and MnO_2 . The distribution coefficient of cobalt shows a considerable enrichment in sediments at stations IV in summer, III, I in autumn and IV in spring of 26.7×10^3 , 26.3×10^3 , 22.2×10^3 and 9.3×10^3 , respectively. However, lower values of 0.39×10^3 and 0.494×10^3 at stations IX and X in spring and of 0.5×10^3 at station VII in autumn are given. The higher Kd values indicated stronger sorption of cobalt to the sediment where cobalt is adsorbed to the surfaces of Fe_2O_3 and MnO_2 .

Lead in sediments is chemically precipitated from surface water solution, and the remainder has been transported in detrital particles. However, lead occurring in sediments has two distinct mineral associations, one with the clay minerals and the other with authigenic minerals and/or biogenous debris. The lead concentrations in sediments of Lake Edku are between a minimum of 0.89 mg/kg at station III in spring and summer to a maximum of 3.4 mg / kg at station I in spring. The seasonal average values are given in the order: $1.98 > 1.88 > 1.80 > 1.58$ mg/kg for winter, autumn, summer, and spring, respectively. The higher value observed in winter is due to the effect of rain water to dissolved atmospheric lead, which adsorbed on Fe_2O_3 and $\text{Fe}(\text{OH})_3$ causing an increase of its concentration in sediments. The annual average value of lead concentration in sediments of Lake Edku showed a minimum of 1.15 mg/kg at a station III and a maximum of 2.41 mg/kg at a station I. The value of 2.15 mg/kg is observed at a station IX.

The higher value at station I is due to the effect of sea sediment transfer to the Lake which may affected by the mining process and many other industries (Aboul Naga, 2000). The positive correlation coefficient between Pb and Fe concentrations ($r = 0.156$) depicted that Pb is effectively adsorbed from the sea water by hydrous ferric oxide.

There are many major specific sources on the worldwide basis for Cadmium such as atmospheric deposition, smelting and refining of nonferrous metals, manufacturing processes related to chemicals and metals, and domestic waste water (Huzinger, 1980). Cadmium concentrations in Lake Edku are ranged from a minimum value of 0.22 mg/kg at a station III in summer and a maximum of 2.10 mg/kg at a station IX in spring. The seasonal average

variation of cadmium in Lake sediment is ranged in the orders $1.26 > 1.17 > 0.99 > 0.98$ mg/kg for spring, winter, summer and autumn, respectively. So, adsorption of cadmium on the surface of Fe and Mn oxides and hydroxides occurs (Dossis et al, 1980). The annual average variation of cadmium concentrations in sediments is between a minimum of 0.62 mg/kg at station III and a maximum of 1.56 mg/kg at station IX. The highest cadmium concentration in the eastern part of the Lake is attributed to the effect of drain and wastewater, at eastern part beside the use of phosphate fertilizers. The positive correlation between Cd and Fe in sediment ($r = 0.238$) is attributed to adsorption of Cd on $\text{Fe}(\text{OH})_3$ and Fe_2O_3 (Dossis et al, 1980). The higher Kd for Cd values indicated the stronger the sorption of Cd to the sediments.

The primary source of chromium includes domestic wastewater, manufacturing processes, involving metals and the dumping of sewage sludge (Beltagy, 1973, Nriagu et al, 1989). Chromium concentrations in Lake sediments are fluctuated between a minimum of 30 mg/kg at station VIII in summer to a maximum of 75.2 mg / kg at station X in spring and station V in summer. The seasonal average concentration of chromium in Lake sediments is given in the order: spring > summer > autumn > winter of 66.45, 52.97, 51.31 and 45.35 mg/kg, respectively. The higher values are associated with maximum average seasonal value of Fe and Mn. It has shown that chromium is effectively adsorbed from seawater by hydrous oxides of manganese, nickel and cobalt. The annual average variations of chromium in Lake sediment are between a minimum value of 45.83 mg / kg at a station II to 60.31 mg / kg at a station VII. The higher values given for eastern part is attributed to the effect of drain water (Aboul Naga, 2000). Under oxidizing conditions, chromium transformed to chromium (6+) oxidation state, and result in partial loss from the sediments. Hexavalent chromium is generally moderately toxic to algae and other aquatic plants (U.S Minerals Yearbooks Bureau of Mines, 1989).

The major source of Nickel is discharge of municipal wastewater followed by smelting and refining of nonferrous metals (U.S Minerals Yearbooks Bureau of Mines, 1989). The concentrations of nickel are varing between 11.10 mg/kg at station III in summer to 20.31 mg/kg at stations IV and V in the same season. The seasonal average variations are given in the order: $15.76 > 15.15 > 14.46 > 14.04$ mg/kg for spring, summer, winter and autumn, respectively. The higher value of Ni is associated with Fe and Mn due to that Ni has been scavenged directly from water by hydrous MnO_2 . Also, nickel is contained in ferromanganese minerals and some of nickel is likely to be contained in the clay minerals. The annual average values of nickel concentration are between a minimum value of 13.79 mg/kg at station IX to 18.35 mg/kg at station V.

This is attributed to the release of nickel from sediments at eastern part than at western region (Aboul Naga, 2000). Total Ni residues in aquatic plants may affect its growth in addition to its effect on fish. The positive correlation coefficients ($r = 0.481, 0.260$) between Ni and both Fe and Mn is attributed to coprecipitation of nickel from Lake water by $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The linear relationship between Ni and Mn may be due to scavenging of the former from surface water by $\text{MnO}_2 \cdot x\text{H}_2\text{O}$. Positive correlation between Ni and the organic matter ($r = 0.300$) in the absorbent sediment of Lake Edku is deduced. This indicates the existence of relatively high concentrations of nickel in organic rich sediments (Aboul Naga, 2000).

Conclusion

The constituents of Lake Edku water may be compared with levels of different criteria (WHO, 1993, EPA-EU, 2001 and Egyptian chemical standards, 1994), Table (3). The maximum permissible limits are recorded. Most of the studied constituents are within the permissible element limits. The Lake is polluted by iron and manganese according to WHO, EPA and EU standards while it considered as unpolluted Lake with the same elements according to Egyptian standards. Lake water is considered as polluted water with Cd and Cr according to all of the above four standards, Table (3).

Table 3: Standard Limits of Drinking Water Parameters (Maximum Permissible Limits) According to Different Criteria

Parameters	WHO	EPA	EU	Egyptian
PH	6.5-8.5	6.5-8.5	6.5-8.5	6-9
Cond., $\mu\text{S}/\text{cm}$	-	-	400 GV*	-
Colour	-	15 units	-	-
TDS, mg/L	1000	500	500	1500
PO_4^{3-} , mg/L	0.3	-	-	0.3
SO_4^{2-} , mg/L	400	500	250	400
Cl^- , mg/L	250	250	250	600
NO_3^- , mg/L	45	45	-	45
Ca, mg/L	200	-	100 GV	200
Mg, mg/L	150	-	50	150
Na, mg/L	200	-	150	-
K, mg/L	-	-	12	-
Al, mg/L	-	0.05-0.2	0.2	-
B, mg/L	0.3	-	1 GV	-
Fe, mg/L	0.3	0.3	0.2	1
Mn, mg/L	0.05	0.05	0.05	0.5
Cu, mg/L	1	1	0.1	1
Zn, mg/L	5	5	0.1 GV	5
As, mg/L	0.01	0.01	0.05	0.05
Cd, mg/L	0.005	0.01	0.005	0.01
Cr(total), mg/L	0.05	-	0.05	0.05
Hg, mg/L	0.001	-	0.001	0.001
Ni, mg/L	-	0.1	0.05	0.1
Pb, mg/L	0.05	0.005	0.05	0.05
Se, mg/L	0.02	0.05	0.01	0.01

WHO 1993; US EPA 2001; EU 1997; ECS, 1994; GV*: Guide val

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