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DISTRIBUTION OF SOME METAL CONCENTRATIONS IN WATER AND SEDIMENTS OF LAKE EDKU, EGYPT

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The heavy metals concentrations, Fe, Mn, Cu, Zn, Pb, Cd, Cr, Co, Ni, give small variations between all stations in the different seasons. Most of the higher values are recorded at the stations, which receive drain water. Organic matter, carbonate, phosphate, calcium, magnesium, and the heavy metals were analyzed in sediments. The contents of organic matter 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 seasons. Manganese concentrations show its maximum in spring and its minimum in winter. Copper is of high content 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 concentration of cadmium points to drain water is of high level. The behavior of chromium and nickel was explained from its adsorption on the surface of iron and manganese oxides due to existence of higher values of Cr and Ni with higher values of Fe and Mn. The high content of Cr was recorded in spring season.

Keywords: metal concentrations; sediments; Lake Edku; Egypt

INTRODUCTION

The hydrography of the Nile Delta including Lake Edku has changed to a great deal during the early ages. It can be considered as shallow brackish water basin of about 17 km long and 6 km wide. It receives drain water from three main drains (Edku, Bousily and Berzik).

Lake Edku is situated in the north of the Nile Delta, west of the Rosetta branch between longitude 30° 8' 30" and 30° 23' 00" E and latitude 31° 11' 00" and 31° 18' 00" N. It extends for about 17 km in the east-west direction. The width of the lake (N-S direction) is about 11 km at its widest part, where the narrowest part is only about 5 km. The lake is connected to the sea (at the village of Maadiya) near to its northwest end through a short channel called "El-Boughaz". The total area of the lake is decreased from 30.000 to about 12.000 ha as a result of agricultural reclamation. The lake water receives agricultural drain water at its eastern section where two main land drains pour their water through hydraulic pumps.

Berzik and Edku-Bousily drains supply water to the lake. The depth of the lake fluctuates between 60 and 150 cm with an average of about one meter.

The lake is connected to the Mediterranean at its northwestern part. An amount of $3.3 \cdot 10^6$ m^3 per day of brackish water is introduced into Abu Qir bay from Lake Edku throw Boughaz El Maadiya. The land drains contribute to a relatively enormous flow of drain water ranging from 25.0 to 95.3 million cubic meters per month.

The main goal of the present study is to detect the status of Lake Edku especially the distribution of the metals in water and sediments to improve the lake status in the future.

MATERIALS AND METHODS

Sampling stations

El–Maadiya region: Stations I and II are situated near El-Boughaz, which represents the area of the lake – sea connection. These areas are occasionally affected by the seawater entering the lake through El-Boughaz. *Western region:* Station (III) lies to the west at Geziret El-Nagaa, which is affected by the seawater entering through El-Boughaz. Station (IV) is shallow with depth ranging between 45 – 100 cm. *Middle region:* Station (V) is located in the south western part of the lake, and is densely covered with Potamogeton Pectinatus. The area is sheltered and not affected by seawater. Station (VI) is located at the middle of the lake. It is completely clean from macrophytes. A permanent slow stream of water drain current that is flowing from the east to the west part affects this area. This may agitate in certain periods the bottom mud. Station (VII) is situated in the south part of the lake with the existence of macrophytes. *Eastern region:* Station (VIII) is situated in the eastern side near the drains and is directly affected by drain water introduced through Edku and Bousily drains. Station (IX) is situated to the east near Geziret El-Mayet. It is covered with the common macrophytes. The station is directly affected by drain water. Station (X) lies in Lake Ghitas, which is mainly affected by the Berzik drain.

Sample collection and analysis

For the period from May 2001 to April 2002, water samples were collected seasonally from ten stations covering Lake Edku (Fig. 1) and kept in well-stoppered polyethylene plastic bottles. Fe, Mn, Cu, Zn, Pb, Cd, Cr, Co and Ni were determined by atomic absorption spectrometer according to standard methods.

Sediment samples were collected from ten stations covering Lake Edku using the Ekman grab sampler and kept in polyethylene bags; sediment samples were washed with distilled water and dried at 85°C in an oven, then ground in an agate mortar.

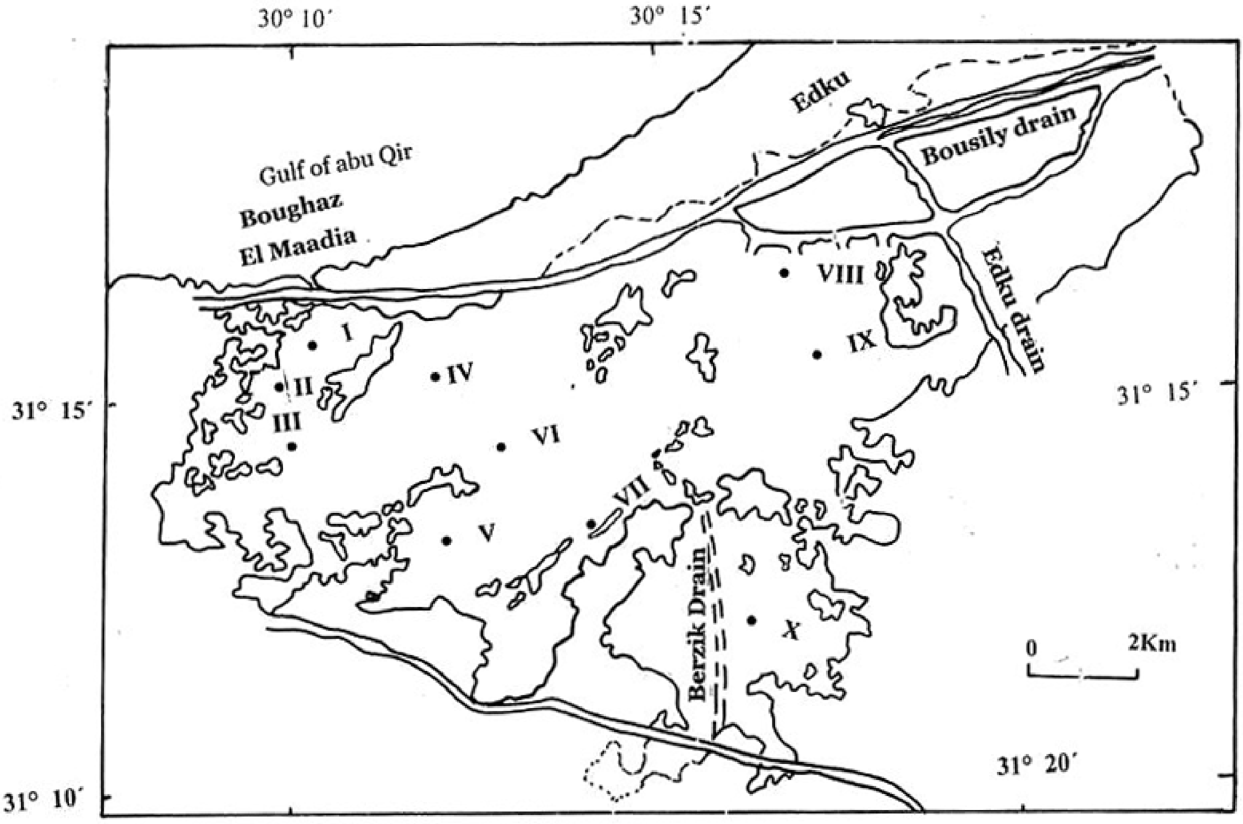

Fig. 1. Map of location of sampling stations of Lake Edku

Sediment analysis

Organic matter (%) was determined according to the method given in Ref. [1] using oxidation behavior technique. Carbonate was determined by the acid-base titration procedure. Total phosphorus was determined according to standard methods [2].

Trace metals in sediments were expressed as ppm (μg/g) except for iron, where it is expressed as mg/g due to its high concentrations in the sediments. The data for Lake Edku water and sediments are collected in Tables 1 and 2, respectively.

Statistical analysis

The obtained data analyzed statistically lead to understand aspects of the chemical and physical processes prevailing in the lake system. Correlation coefficients were calculated between all pairs of measured variables, using the SPSS program.

Table 1

Maximum and minimum values of seasonal, seasonal average and annual average of the chemical parameters of Lake Edku water

Parameters Values		Fe mg/l	Mn μg/l	Zn μg/l	Cu μg/l	Cd μg/l	Cr μg/l	Co μg/l	Pb μg/l	Ni 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

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^- 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

RESULTS AND DISCUSSION

Heavy metals in water

Iron

Most ferrous compounds in aquatic environments resulting in iron precipitate in alkaline and oxidizing conditions [3]. The seasonal average values of dissolved iron concentrations varied from the maximum value of 1.21 mg/l at stations III and IX during spring to a minimum value of 0.03 mg/l at station VI during summer. This may be related to the low level of dissolved oxygen with pH > 7 to precipitate $Fe(OH)_3$ in summer. High concentration of oxygen leads to iron oxidation and subsequent hydrolysis to form insoluble $Fe(OH)_3$ according to the following reactions:

$$2Fe^{2+} + \frac{1}{2}O_2 \xrightleftharpoons{H^+} 2Fe^{3+} + H_2O$$

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

The negative correlation coefficient (r = –0.307) between dissolved iron and pH, supports the above suggestion.

The seasonal average values are ranged in the order: spring > winter > autumn > summer: 0.67 > 0.57 > 0.52 > 0.19 mg/l, respectively. The higher values may attribute to the high amount of total susbended solids, TSS, that contains a large amount of iron with positive correlation (r = 0.326) between iron and suspended matter. The low seasonal average iron content in summer is possibly due to the consumption of iron by phytoplankton which increased in summer and decreased in autumn [4]. The removal of iron and other trace elements from the water system by planktonic organisms may take place through: 1) assimilation by organisms and subsequent transport as fecal material, and 2) body adsorption [5].

The annual average value of iron is fluctuated between 0.30 mg/l at station VIII and 0.82 mg/l at station I. The maximum value is obtained for the western part in which the iron concentrations increased as a result of the presence of iron used in building the international coastal road in the northwestern part while the minimum value is obtained at station VIII due to the dilution of the lake water by agriculture and drain water sources.

The highly significant correlation (r = 0.545) between the concentrations of iron and manganese suggests that the association of the two elements originates from a common source and also during transportation and/or deposition reactions [6].

Manganese

The minimum value of 18 μg/l is recorded at station V during autumn, and the maximum value, 112 μg/l, is recorded at station IV during winter.

The seasonal average of manganese concentrations at autumn and winter were higher than that of spring and summer and varied in order: 67.50 > 62.31 > 53.71 > 47.18 μg/l for autumn, winter, spring and summer, respectively. The seasonal average values in autumn and winter were higher than those of spring and summer which can be due to the increased consumption of this element by the phytoplankton, in spring and summer than autumn and winter [7]. The low manganese content in the lake explains the contribution of phytoplankton, pH and dissolved oxygen contents.

The maximum annual average values of Mn, 75.25 μg/l, is obtained at station I, while the minimum amount, 28.83 μg/l, recorded at station V in the middle of the lake. This may be due to the effect of dilution of the lake water and to the abundance of phytoplankton. On the other hand, the higher concentrations measured at the northwestern stations of the lake could be due to the presence of higher concentrations of the suspended matter. The annual average values of dissolved manganese are given, where the maximum is assigned at station I accompanied by the maximum annual average of iron due to the precipitation of their hydroxides at the bottom. The highly significant positive correlation (r = 0.526) between manganese and iron concentrations is probably due to their association as oxides and hydroxides [8]. The toxicity of manganese is relatively low. The permissible levels of manganese in water used for domestic purposes are quite low, and <0.05 mg/l, due to laundry and bathroom fixtures stained by very low levels of manganese in water, and the maximum acceptable concentration in water for continuous irrigation is 0.2 mg/l [9].

Zinc

It is one of the biologically significant known elements [10]. It exists in sea water in submicromolar concentrations [11]. It has been reported that organic complexation controls the concentration of dissolved zinc in aquatic environment [12]. Zinc is essential for growth of marine organisms and its concentration affected by plankton communities [13].

The kinetics of removal of Zinc in aquatic systems are strongly affected by the rates of biological processes. It is also a common pollutant found in several industrial effluents such as those produced by textile, basic chemicals, electroplating, motor and other industries. The seasonal and regional variations of total zinc in the lake water show that the dissolved zinc concentration in lake water is fluctuated between a maximum, 126 μg/l, at station VII during autumn and a minimum, 11.0 μg/l, at station IV in summer. A maximum seasonal average value of zinc, 52.6 μg/l, was recorded in autumn while a minimum, 21.7 μg/l, was recorded in summer. The annual average values ranged between a maximum, of 57.55 μg/l, at station VII and a minimum of 8.85 μg/l, at station IX.

Zinc is positively correlated with iron, manganese and copper (r = 0.267, 0.290 and 0.286, respectively). This correlation may point to the adsorption of zinc, manganese, and copper by hydrous iron oxides [14].

Copper

The copper complexation in water is affected by dense phytoplankton blooms [15], and is strongly verified in spring. Copper speciation is influenced by biological and geological processes [15]. Its maximum values fluctuate between 49.0 μg/l at station VII during spring and 14.0 μg/l at station X during winter. The seasonal average variations of copper vary between 32.1 μg/l for spring season compared to the lower value of 19.8 μg/l during summer. The lower values are mainly attributed to the uptake copper by the living organisms. For annual average copper concentrations, the maximum and minimum values of 31.50 and 20.0 μg/l are 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 [16].

The data could be speculated that the source of the dissolved copper in water may be outlined to remobilization from sediments. However such approach could be subjected to further steps, mainly of adsorption and coprecipitation phenomenon of dissolved species on to suspended matter [17].

Cadmium

Cadmium is extremely toxic to fish. Its effects on the growth rate have been observed even for concentrations between 5 and 10 μg/l [18]. Phytoplankton are likely to play a more significant role in scavenging of cadmium than they play in the removal of other metals [19].

The maximum concentration of cadmium is 16.0 μg/l at stations II and X during winter and summer, respectively, while the minimum concentration of 2.0 μg/l is given at stations VIII and IX during winter and spring, respectively. The minimum values are attributed to the effect of Edku – Bousily and Berzik drains on the lake water. The seasonal average concentrations of cadmium are 8.5 μg/l in autumn and 7.6 μg/l in winter, probably due to the dilution in winter as a result of rain fall [20]. The maximum value is due to high oxygen concentration with average (10.75 mg/l) which oxidizes the cadmium [20]. The higher and lower annual average concentrations of cadmium are observed of 11.75, 11.25, and 10.00 μg/l at stations X, II, and I, respectively, while the minimum value of 4.0 μg/l is observed 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 of that station.

Chromium

Chromium is one of the biochemically active transition metals in aquatic environment. Its concentrations gave minimum and maximum values fluctuated between 1.0 and 26.0 μg/l recorded at stations VIII and II during summer season, respectively.

The seasonal average values of chromium concentration are fluctuated between the maximum value of 11.1 μg/l in winter and 9.7 μg/l in summer. The seasonal average values in autumn and winter of (10.2 and 11.1μg/l) are higher than those of spring and summer of (9.9 and 9.7 μg/l), due to the consumption of chromium by phytoplankton that is higher during spring and summer than autumn and winter [7].

The maximum and minimum annual average chromium concentration values are 16.5 and 2.5 μg/l recorded at stations II and VIII, respectively. Meanwhile, the chromium concentrations are higher in the western part due to the effect of the seawater which is affected by many industrial wastes such as Abu Qir fertilizer company, as illustrated in the lake near El-Boughaz. The negative correlation between chromium and phosphate ($r = -0.372$) is a result of precipitation of chromium phosphate [17].

Cobalt

Cobalt is a very important element in aquatic environment. It is moderately toxic to most aquatic species more than Cr^{3+} and Cr^{6+} but much less toxic than Cd^{2+} and Cu^{2+}. Cobalt occurs in low concentrations in marine waters, often below 10 ppm. Higher levels of cobalt have been recorded in the open ocean, but these are probably due to contamination with phytoplankton and other organisms that metabolize vitamin B12.

The present results indicated that the cobalt concentrations in lake water fluctuated between a maximum value of 23.0 μg/l at station I during summer and a minimum value of 1.0 μg/l at stations IV and III during summer and autumn, respectively.

The seasonal average variation of cobalt concentration is fluctuated between 7.6 μg/l in autumn to 10.70 μg/l in spring, may attribute to contamination of cobalt with phytoplankton that occurs in a large quantity in spring season [21].

The maximum and minimum annual average variations of cobalt, are 14 μg/l recorded at station I and 5 μg/l observed at stations III and VIII, respectively. The annual average values of total dissolved cobalt gave a maximum amounts assigned at station I accompanied by the maximum annual averages of iron and manganese to suggest the formation of hydroxides precipitates to the bottom or may form different complex structures with many organic ligands [19].

On the whole, the number of toxic effects has been reported following the long-term exposure of fish to cobalt [19]. Generally, cobalt occurs in extremely low concentrations in surface waters, but most nations have not promulgated regulations aimed at protecting fish and other aquatic species.

Lead

Lead is very important in the aquatic system; it is used for many industrial purposes such as storage batteries, metal products, pigments and chemicals. Total Pb is often found in high concentrations in aquatic plants, particularly those growing in freshwater and receiving other or mine industrial wastes [22]. The present results indicates that the maximum value of 225 μg/l is recorded at station III in spring, while the minimum of 10 μg/l recorded at station II during spring and summer. The seasonal average variation of lead is fluctuated between 46.1 μg/l during autumn and 89.4 μg/l during spring. The datum is of typical anthropogenic and urban activities [23], and accumulation in plants and phytoplankton. The annual average value of lead is fluctuated between 18.5 μg/l at station II to 95.5 μg/l at station VI. The higher Pb content in the middle part of the lake is probably due to the effect of domestic drain water from Berzik and Edku-Bousily drains, which contains large concentrations of Pb. The concentration of Pb is affected by many factors: many small inflows, heavy rain, uptake by zoo- and phytoplankton [24].

Nickel

It results from industrial and urban activities [23] and may accumulate in many types of fishes and macrophytes. The concentrations in water of Lake Edku are ranged from minimum, 16.0 μg/l, at stations VIII in winter, to maximum, 110 μg/l, at station IV in winter. The seasonal average nickel concentrations are 40.9 > 36.9 > 32.4 > 31.0 μg/l for spring, summer, winter, and autumn, respectively. The high seasonal average nickel concentrations in summer and spring are probably attributed to contamination of nickel with phytoplankton that occurs in a large quantity during spring season [21]. The annual average variations of nickel concentrations are fluctuated between 26.25 μg/l at station VI and 51.5 μg/l at station IV. The lower value is probably attributed to release of nickel from sediment at station VI in the eastern part of the lake in addition to the effect of drain water discharge. Total Ni residues in aquatic plants may affect its growth in addition to its effect on fish [24].

Analytical results on the lake sediments during 2001–2002

Organic matter

The composition and structure of the organic matter in the sediment are varying due to its origin and geological history in the marine and aquatic environment. Phytoplankton and zooplankton are the most abundant sources of the organic material in the sediments [25]. The organic matter content of the sediment is a result of the contribution of terrigenous materials and the decomposition of plants and animals by the action of bacteria [26]. The organic matter concentrations are ranged from the highest value of 10.13 % at station III during summer to the lowest value of 3.26 % at station VI during winter.

The seasonal average organic matter concentrations are fluctuated between a maximum and minimum values: of 5.85 % in summer and 5.02 % in autumn, respectively. The high organic matter value recorded in summer is attributed to the high value of drain water. The high rate of phytoplankton growth together with the organic detritus introduced by the drainage system can be considered as the main source of organic matter in the lake. 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 contents of organic matter are 4.66 % at station II and 6.09 % at station V. The former may be attributed to the decomposition of organic matter in the sediments more than that of the latter with the enrichment of sediments with organic matter coming from the drain water.

A major anthropogenic source for organic matter to the lake is the lake-sea connection where cellulose remains derived from Racta and National Paper Mills discharging into Abu-Qir Bay invading the west-north region of the lake. In general, the higher values of seasonal average variations of organic matter 5.77, 5.85 %, recorded in spring and summer, respectively, may attribute to increase chlorophyll-a content of the surface sediment during these seasons. The quantitative distribution of organic matter content in the lake sediments depends principally on some factors [27]:

1) The allocthonous organic load entering the lake with sewage and industrial wastes.

2) The autochthonous organic production of the lake sediments.

3) The intensity of decomposition of organic matter.

4) Particle composition of the sediments.

The statistical correlations indicate that the organic matter are highly correlated with some metals in the lake sediments, probably due to the organic matter associated with sediment particles. This is largely responsible for the ability of sediment to adsorb the metals [28].

A positive correlation coefficient is recorded between organic matter and carbonate in lake sediment (r = 0.283). This is mainly due to the fermentation process, which may occur to the sinking dead materials yielding organic matter and releasing calcium carbonate to the surface sediment from death calcareous shells [29].

Carbonate

$CaCO_3$ precipitation is controlled by photosynthesis [30]. Although many calcite rich sediments may have a large allogenic source of carbonate, many other lacustrine carbonate sediments are truly endogenic. Their principal constituents have been precipitated directly from the water column [31]. The concentrations of carbonate in lake sediments vary between 11.6 g/kg at station II during winter and 29 g/kg at stations VII during spring, and summer. The seasonal average values of carbonate content in sediments are fluctuated between 19.2 g/kg in winter and 26.3 g/kg in spring. The higher value of carbonate is attributed to the aquatic plants and phytoplankton applied to extract CO_2, and thus promotes precipitation of carbonate with the increase of pH [31, 32].

The annual average concentration values of carbonate are fluctuated 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 probably due to the biogenic precipitation of organite by aquatic organisms building their calcareous shells [33]. The sediments at station IV are enriched with mollusca shells and partly calcareous fragments [34]. The relatively high values are due to the calcium rich water where $CaCO_3$ is precipitated with the increase of pH during photosynthesis [34].

Phosphorous

Both phosphorous and nitrogen are important elements controlling the growth and reproduction of phytoplankton [35]. Phosphorous is necessary to all life because of its functions in the storage and transfer of cell energy and in genetic systems [35]. Adenosine triphosphate is an energy carrier and the presence of phosphate groups in nucleotides and hence nucleic acid underscores the need of living organisms for phosphorous [36]. The values of total phosphorous in the sediments of Lake Edku are fluctuated between a minimum of 0.03 % at station VI during winter and a maximum of 0.71 % at station V during autumn. The latter is probably due to the decrease of decomposition of organic matter [27], and the effect of drain water coming from Edku-Bousily and Berzik drains in addition to agricultural drain or use of phosphate fertilizers. The greatest part of added fertilizers is recorded in soil flooding and eventually it finds its way to the lake through drainage water. In general, the phosphorous supply in drainage water from the agricultural area is about 10 times greater than background [37]. The seasonal average values 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 a sequence is related to drain water and dissolution of phosphorous from sediments to the overlying water, as a result of resuspention of sediments by winds and boat movements. The annual average value of phosphorous concentrations are 0.48, 0.33, 0.33% at stations V, IX, X, respectively, and may be due to the use of inorganic fertilizers washed down from the cultivated land reaching the lake through the drainage system [26]. However, the phosphorous compounds are also present mainly in the waters as dissolved substances. These are extracted from the solution and utilized for feeding by different organisms to death, fall and accumulate at the bottom. These lead to an increase of the phosphorous content in sediments until released again into solution by the action of bacteria [27]. The positive correlation coefficient ($r = 0.19$) obtained between the organic matter and phosphorous in the lake assigned that the domestic sewage is discharged directly to the lake. This is considered as the main source of organic materials including phosphorous [26]. 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 are formed between the metal ions and phosphate in the bottom water adsorbed onto Fe and Mn oxides and hydroxides in the bottom sediments.

Heavy metals in 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 [38].

The chemical forms and the regulatory process that limit solubility lead to bioavailability of metals in sediment – water systems as follows:

1) Metal precipitation as insoluble sulfides in reduced sediment environments [30].

2) Metal adsorption or coprecipitation with colloidal hydrous oxides of iron and manganese, primarily in oxidized environments [40].

3) Metal-complex formation with insoluble humic materials [41].

Iron

The total iron concentrations in the lake sediments are fluctuated 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 attribute to resuspention of sediment with their adsorbed pollutants [42].

The seasonal average variations of 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 attributed to a large amount of organic matter (5.77 %), human activities accompanied with an increase of the amount of domestic discharge from boats [43]. The high value recorded in autumn may also attribute to the 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 [43].

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 [43].

The annual average value of iron content in the lake sediment is fluctuated 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 the 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 [44].

The positive correlation also 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 [45].

$$SOH + M^{Z+} (aq) \leftrightarrow SOM^{Z-1} + H^+ \qquad (1)$$

where SOH assigned a singly protonated surface oxide site and M represents a cationic adsorbate.

The influence of the solution pH and the concentration of adsorbent on the adsorption reaction can be identified from equation (1), where increasing the pH or adsorbent, SOH, concentration increases the sorption of cations.

A positive correlation coefficient ($r = 0.622$) is observed between iron and phosphate content in sediments. The adsorption of phosphate ions on both iron oxide and manganese dioxide is not a simple reaction. Phosphate ions adsorbed on to the surface of these oxides can no longer stay at the adsorption sites [46].

The inorganic phosphate ligand is complexed with the hydrous ferric giving:

$$Fe_x\,(OH)_{3(x-y)}\,(PO_4)_y\,;\,Z(H_2\,O)].$$

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 [47]. The sediment ability to accumulate trace metals under oxygenated and anoxic conditions is evaluated using the distribution coefficient, K_d, term.

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

The concentrations are in ppm units. The maximum and the minimum K_d values of iron are $1.061 \cdot 10^3$ and $0.020 \cdot 10^3$ at stations, VI and I during summer, respectively.

In general, the higher K_d, the stronger the sorption of the metal to the sediments [48].

Manganese

Manganese is found in minerals mostly as carbonates, oxides, silicates and sulphides. It may occur as a particulate manganese or precipitating coating on mineral species, organic matter, and iron-manganese hydroxides. Total manganese concentrations in the lake sediments are given.

The manganese content in the lake sediment is fluctuated between a minimum of 113.00 mg/kg at station I during summer and a maximum of 502.11 mg/kg at station III during spring. There are variations in the concentration of manganese in the lake sediment, probably due to the variation in the grain size of the sediments where the clay sediments are enriched in manganese [26].

However, the seasonal average variations of Mn recorded show that the values are fluctuated 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 the increasing amount of dissolved oxygen in water, which leads to oxidize manganese in water to solid MnO_2 precipitated to the bottom sediment.

The annual average value of manganese concentration is fluctuated 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 the muddy nature of the sediment at these locations [49].

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 [50].

Also, manganese in the lake sediments is associated with phosphorous where the positive correlation coefficient (r = 0.392) is detected and is attributed to adsorption of phosphorous by Fe/Mn oxide in the sediment [6] as well as phosphate is often present in domestic or industrial wastes. In addition, phosphate forms a strong complex with hydrated manganic hydroxide with formula $Mn_x(OH)_{4(x-y)}(PO_4)_y\ ;\ ZH_2O)$ [47]. Based on K_d values for manganese, the highest value of $19.15 \cdot 10^3$ recorded at station III during summer indicated the high sorption of manganese in the middle of the lake. The minimum K_d value of $1.17 \cdot 10^3$ recorded at station I during summer is due to the lower concentration of oxidized manganese in the sediment, where the amount of dissolved oxygen decreases in summer.

Zinc

The zinc concentrations in the lake sediments are vary between 17 mg/kg at station V and 102 mg/kg at station I during spring. The maximum value is mainly due to the effect of the 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 value of 63.93 mg/kg in spring. The relatively high value may attribute 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 [51].

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 value of 52 mg/kg at station VIII.

In general, the concentrations of Zn 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 the west side and the effect of drain water entered to the lake, in addition to industrial and agricultural activities along the eastern and northern parts of the lake [21]. The lowest annual average of 52 mg/kg at station VIII, is mainly due to the lowest K_d values of 0.672 to 2.34, i.e. low sorption of zinc in the sediment [48].

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 [52]. The distribution coefficient of zinc, K_d, is a maximum of $8.455 \cdot 10^3$ at station IV during summer and a minimum of 0.347 at station V during spring.

Copper

Copper is generally introduced to the lake as two main forms: the lithogenic and biogenic [48]. Lithogeic 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 [48].

Metal pollutants also enter the environment from industrial mining effluent, combustion of fossil fuels, discharge of sewage sludge, fertilizer and pesticide residue.

Copper concentration values are ranged from a minimum of 0.8 mg/kg at station III during summer to a maximum of 3.11 mg/kg at station I during 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 the Fertilizers Company. The higher values recorded at the 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. Generally, the copper concentrations in Lake Edku sediments vary as a function of texture and proximity to potential contamination sources.

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 indicate that association of metals with clay minerals or the adsorption of copper on iron oxides occurrs 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 [42]. The distribution coefficient, K_d, of copper shows a minimum of $0.047 \cdot 10^3$ at station VII during autumn, and a maximum of $0.178 \cdot 10^3$ at station VII during summer. The higher K_d values indicate stronger sorption of copper to the sediment where Cu is strongly adsorbed to the surface of manganese oxide.

Cobalt

In the present study cobalt concentrations are fluctuated between a minimum of 5.1 mg/kg at station IX during summer and a maximum of 37.1 mg/kg at a station IV during 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 $Co(OH)_2$ and $CoCO_3$. The positive correlation between cobalt and phosphate (r = 0.107) in the lake sediments, is due to the existence of charged clay particles and anions [42]. However, the correlations between Co and Fe, Mn, Zn are (0.288, 0.330, and 0.226), respectively indicate the association of the metals with clay minerals or the adsorption of both Co and Zn on theFe_2O_3 and MnO_2.

The distribution coefficient of cobalt shows a considerable enrichment in sediments at stations IV during summer, III, I during autumn and IV during spring of $26.7 \cdot 10^3$, $26.3 \cdot 10^3$, $22.2 \cdot 10^3$ and $9.3 \cdot 10^3$, respectively. However, lower values of $0.39 \cdot 10^3$ and $0.494 \cdot 10^3$ at stations IX and X in spring and of $0.5 \cdot 10^3$ at station VII during autumn are given. The higher K_d values indicate stronger sorption of cobalt to the sediment where cobalt is adsorbed to the surfaces of Fe_2O_3 and MnO_2.

Lead

Lead in sediments is chemically precipitated from the 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 fluctuated between a minimum of 0.89 mg/kg at station III during spring and summer to a maximum of 3.4 mg/kg at station I during 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 $Fe(OH)_3$ causes 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 station III and a maximum of 2.41mg/kg at a station I. The value of 2.15 mg/kg is observed at station IX.

The higher value at station I is due to the effect of sea sediment transfer to the lake which may be affected by the mining process and many other industries [33]. 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.

Cadmium

The major specific sources on the worldwide basis are atmospheric deposition, smelting and refining of nonferrous metals, manufacturing processes related to chemicals and metals, and domestic waste water [21]. Only about 15 % of atmospheric deposition comes from natural sources. Cadmium concentrations in Lake Edku are ranged from a minimum value of 0.22 mg/kg at station III during summer and a maximum of 2.10 mg/kg at station IX during spring. The seasonal average variation of cadmium in the lake sediment is ranged in the orders of 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 [53]. The annual average variation of cadmium concentrations in sediments is fluctuated 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 the eastern part besides the use of phosphate fertilizers.

The positive correlation between Cd and Fe in sediment ($r = 0.238$) is attributed to adsorption of Cd on $Fe(OH)_3$ and Fe_2O_3 [53]. The higher K_d for Cd values indicated stronger sorption of Cd to the sediments.

Chromium

The primary source of chromium includes domestic wastewater, manufacturing processes, involving metals and the dumping of sewage sludge [44].

Atmospheric fallout is an important source of chromium in the surface water, from anthropogenic sources and windborne soil particles [54]. Chromium concentrations in the lake sediments are fluctuated between a minimum of 30 mg/kg at station VIII during summer to a maximum of 75.2 mg/kg at station X during spring and station V during summer.

The seasonal average concentration of chromium in the lake sediments is given in the order of: spring > summer > autumn > winter of 66.45, 52.97, 51.31 and 45.35 mg/kg, respectively. The higher values are associated with the maximum average seasonal values of Fe and Mn. However, chromium in clays is strongly concentrated in the size fraction which contains ferromagnetisias minerals, and to lesser extent in the clay fraction. It has been shown that chromium is effectively adsorbed from seawater by hydrous oxides of manganese, nickel and cobalt. The annual average variations of chromium in the lake sediments are fluctuated between a minimum value of 45.83 mg/kg at station II to 60.31 mg/kg at station VII. The higher values given for the eastern part are attributed to the effect of drain water [33].

Under oxidizing conditions, chromium transforms to chromium (6+) oxidation state, and results in partial loss from the sediments. Hexavalent chromium is generally moderately toxic to algae and other aquatic plants [55].

Nickel

The major source of discharge is the municipal wastewater followed by smelting and refining of nonferrous metals [55].

The concentrations of nickel are varying between 11.10 mg/kg at station III during summer to 20.31 mg/kg at stations IV and V during the same season. The seasonal average variations are given in the order of: 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 the fact that Ni has been scavenged directly from water by hydrous MnO_2. Nickel is also 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 fluctuated between a minimum value of 13.79 mg/kg at station IX to 18.35 mg/kg at station V. This is attributed to a greater release of nickel from sediments at the eastern part than at western region [33].

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 the lake water by $Fe_2O_3 \cdot xH_2O$. The linear relationship between Ni and Mn may be due to scavenging of the former from the surface water by $MnO_2 \cdot H_2O$. The positive correlation between Ni and the organic matter (r = 0.300) in the absorbent sediment of Lake Edku is deduced. This points the relatively high concentrations of nickel which exists in organic rich sediments [33].

CONCLUSION

Lake Edku is considered as the most important Nile Delta Lake in fish production (more than 50 % from Egyptian fish production). With much more safe, the constituents of water may be compared with levels of different criteria [56–58] (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 is considered as an unpolluted lake with the same elements according to Egyptian standards. Lake water is considered as polluted water with Cd and Cr according to all above four standards (Table 3). Accordinely we suggest the following recommendations in this context to protect the lake from such pollution:

1) Applying the law 48 (1982) and the law 4 (1994), protection of the River Nile and the water stream from pollution.

2) Construction of special units for treatment and purification of all types of drainage and waste water (agricultural, industrial and domestic).

3) Successive analysis of lake water to assess the amount of pollutants to make suitable decisions.

4) Take an action to prohibit throwing of wastes in the lake.

5) Consumption of the lake water for agricultural, industrial and/or domestic must be under control in order to decrease water pollution.

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., μS/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 value

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Р е з и м е

ДИСТРИБУЦИЈА НА КОНЦЕНТРАЦИИТЕ НА НЕКОИ МЕТАЛИ ВО ВОДИТЕ И СЕДИМЕНТИТЕ ОД ЕЗЕРОТО ЕДКУ, ЕГИПЕТ

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Клучни зборови: концетрација на метали; седименти; езеро Едку; Египет

Концентрациите на некои тешки метали (Fe, Mn, Cu, Zn, Pb, Cd, Cr, Co, Ni) даваат мали варијации помеѓу сите станици во различни сезони. Повеќето од највисоките вредности се забележени кај станиците кои прифаќаат дренажни води. Во седиментите се анализирани органски материи, карбонати, фосфати, калциум, магнезиум и тешки метали. Содржините на органските материи имаат неправилен тренд и се под влијание и на земјоделски активности и активности од домаќинствата. Уделот на карбонатите се зголемува напролет како резултат на зголемената фотосинтеза. Концентрациите на фосфорот се под влијание на потеклото на дренажните води, земјоделските

активности, примената на фосфатните ѓубрива и таложењето на органските материи на површината на седиментите. Концентрациите на цинкот и железото се највисоки напролет и наесен.