World Applied Sciences Journal 24 (3): 282-294, 2013
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2013.24.03.75115

Geochemistry of Some Major and Trace Elements in Sediments of Edku and Mariut Lakes, North Egypt

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Submitted: Jul 1, 2013; **Accepted:** Aug 12, 2013; **Published:** Aug 25, 2013

Abstract: Concentrations of Na, K, Ca, Mg, Li, Bi, Co, Se, B, carbonates, organic carbon and granulometry from 26 sites in Mariut and Edku lakes were studied. The metal concentrations inside Lake Mariut varied from 0.29 to 1.13%, 0.08 to 0.32%, 8.4 to 16.3%, 1.9 to 6.7 %, 17.92 to 116.40 µg/g, 68.59 to 309.79µg/g, 0.63 to 17.19 µg/g, 0.34 to 35.67µg/g and 0.04 to 4.92 µg/g for Na, K, Ca, Mg, B, Li, Co, Bi and Se, respectively. For Lake Edku metal concentrations varied from 0.30 to 1.19%, 0.13 to 0.38%, 4.9 to 16.8%, 1.8 to 7.9 % 21.95 to 66.22 µg/g, 61.00 to 145.94µg/g, 7.43 to 24.79 µg/g for 5.99 to 13.40 µg/g and 0.12 to 1.39µg/g for Na, K, Ca, Mg, B, Li, Co, Bi and Se, respectively. Metal data were normalized against Li in order to determine the level of metal contamination and to detect any anthropogenic contribution of metals to the lakes. The results revealed that all surface sediments in both studied lakes (Co, Bi, Na, K and Ca) are originated predominantly from lithogenous sources confirming their natural origin. While, the sediment are contaminated with Se and B which might be affected by man's activities (municipal discharges, industrial development, agricultural drainage, Fish farms…..etc. Data set obtained for Na, K, Ca, Mg, B, Li, Co, Bi, Se and TOC and TCO_3 in sediments of both lakes are treated using principal component analysis (PCA), which identified four factors responsible for data structure explaining 82.32% of total variance in Lake Edku and 85.95% Lake Mariut.

Key words: Lake Mariut · Lake Edku · Major Element · Trace Element · Enrichment Factor

INTRODUCTION

Coastal zones and lakes are important issues in the international debate for the environmental and sustainable development. They have become the major site for extensive and diverse economic activities [1]. Coastal lakes occupy 13% of worldwide coastal areas and are often subjected to both natural and man-made factors [2]. Importance of many lakes is coming from fishing and salt extraction along their borders [3, 4].

The northern Egyptian lakes represented by the main five lakes (Mariut, Edku, Burullus, Manzalla and Bardawil) are distributed along the northern shoreline of Egypt, from west to east, respectively. All of them, with the exception of Lake Mariut, are directly connected to the sea. They represent 25% of total wetlands of the Mediterranean [5]. The lakes are an important natural resource for fish production in Egypt. Until 1991, these lakes have always contributed than 40% of the country's total fish production, but at present this has decreased to less than 12.22% [6]. The present work focused to study both Mariut and Edku lakes which located west of the Rosetta branch of the River Nile.

Lake Mariut, the smallest of the northern Egyptian lakes, located in the north western coast of Egypt, is a shallow, brackish-water lake located southeast of the highly populated urban areas in Egypt and in the world [7]. Since 1950, the total area of the lake has been reduced to a third of its original size [8]. Lake Edku is the third largest wetland area in the northern delta. It supports a fishery of moderate importance.

Pollution of the lake is as a result of discharge of ever-increasing quantities of agricultural drainage water with heavy fertilizer and pesticide loads to lakes, occasional siltation and closure of Bughaz, expansion of reed swamps and submerged aquatic vegetation and over-fishing [5].

Natural and anthropogenic material accumulates simultaneously in sediments. The problem is exacerbated by the magnitude of the variation in the loading of

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elements originating from these two sources, as well as the interaction of elements with sediment grain size, mineralogy and organic carbon content [9]. Geochemical procedures include normalization in relation to a conservative element such as Al [10], Fe [11], Rb [12] and Li [13]. A normalization procedure is based on the fact that the proportions of the metal in relation to a conservative element are relatively constant in the earth crust [14]. Lithium was used as a reference element in this study. However, most of the previous studies for Lake Mariut and Edku dealing with some the parameters studied in surficial sediments by [15-20]. Regarding these studies little data are available on the level of (Na, K, Ca, Mg, Li, Bi, Co, Se, B, TOC and TCO_3). From this fact, the objective of this study was to examine the relationships of metal concentrations to Li concentrations in order to determine the level of metal contamination in study area and to detect any anthropogenic metal contribution to the lakes.

Study Lakes: Two coastal lakes in the northern part of the Nile Delta were investigated in this study, namely Mariut and Edku Figure (1).

Lake Mariut: Lake Mariut located in the north western coast of Egypt and lies in the southern side of Alexandria City on the Egyptian Mediterranean coast (31° 04¯- 31° 08¯N and 29° 49¯- 29° 56¯E). It had total area of about 65 km^2 with average water depth of about 1 m and the water level was always kept at 2.8 m below sea level. This makes the lake to work as a sink to drain different kinds of drainage waters from neighboring catchment areas of Alexandria City. This Lake has artificially been divided into sub-basins comprising the main basin or lake proper, the fish farm, the northwest basin and the southwest basin Figure (2). The Main Basin, since 1993, receives flow from three main sources: (1) Kalaa (agricultural) Drain that also carries the discharge from a treatment plant called East Treatment Plant (ETP), (2) Directly from the West Treatment Plant (WTP) outlet and (3) Omoum (agricultural) Drain. The other three basins receive flows from a variety of canals and drains but do not receive any effluent from the ETP or WTP.

Lake Edku: Lake Edku is the third largest wetland area in the northern delta. It supports a fishery of moderate importance. It is also of moderate importance for both wintering and breeding water birds [21]. Lake Edku is shallow brackish coastal basin 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 Figure (3). Results of remote sensing mapping of May, 2007 satellite image indicate that the total surface area of the lake is about 62.5 km^2 (~ 15.000 Fadden) of which 22 km^2 is open-water, whereas the rest area (42.7 km^2) is either inhabited by aquatic vegetation or occupied by island and islets. According to these estimates, the open water area represents only about 35%. almost one third of the total surface area of the lake [22]. The lake is separated from the sea through a sand barrier that is occasionally inhabited with salt marshes, Salinas and high dunes. The lake water receives agricultural drain water at its eastern section where two main land drains pour their water through hydraulic pumps. Barsik, Khairy and Edku-Bousily drains supply water to the lake. The depth of the lake fluctuates between 60 and 150 cm

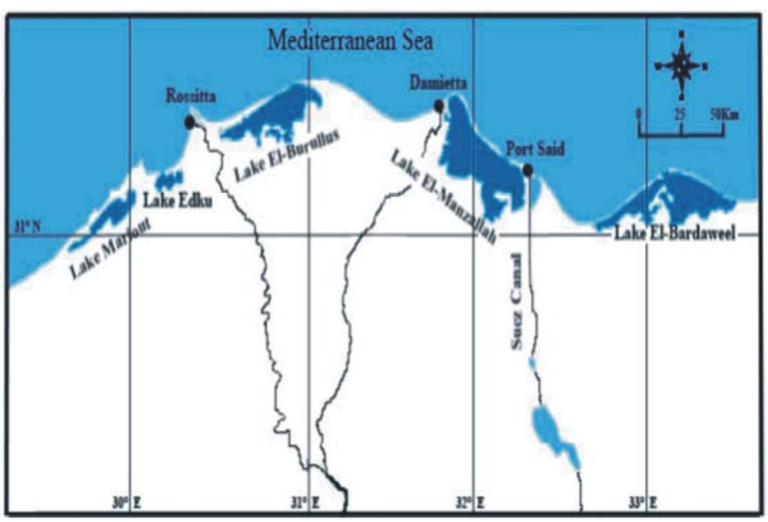

Fig. 1: Map showing location of the two studied lakes; Mariut and Edku

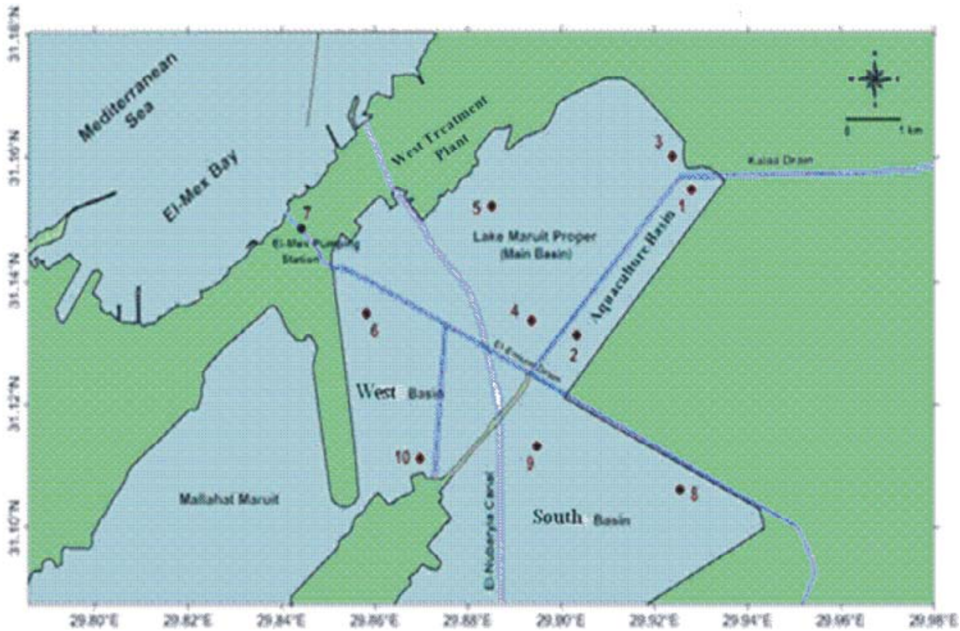

Fig. 2: Map of Lake Mariut showing the sampling stations

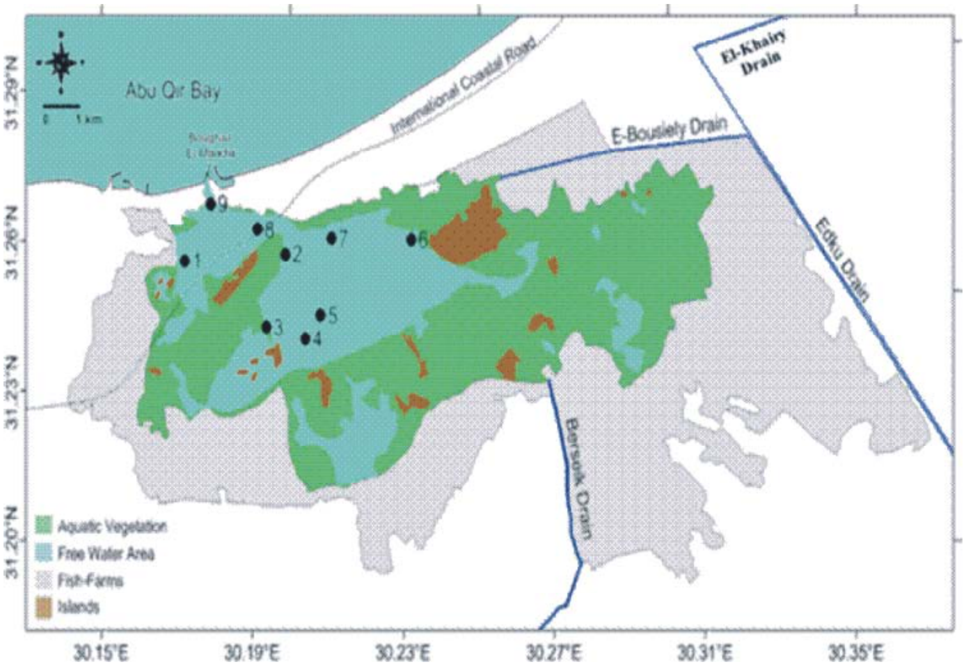

Fig. 3: Map of Lake Edku showing the sampling stations

with an average of about one meter [5]. The El-Khairy and Barsik Drains discharge amounts of drainage waters to the lake. The water sources of El-Khairy Drain are from three drainage waters coming from El-Bousely, Edku and Damanhour sub-Drains, transporting domestic, agricultural and industrial wastes, as well as the drainage water of more than 300 fish farms [18]. Barsik Drain transports mainly agricultural drainage water to the lake. The lake also receives sea water at its north western part through Boughaz El-Maadyia from Abu Kir Bay, which is a shallow basin receiving considerable amounts of raw industrial wastes from several factories through El-Tabia pumping station [23, 24].

MATERIALS AND METHODS

Sampling: During winter 2011 surfacial sediment samples from lake Mariut (n=10) and three from the drains; lake Edku (n= 9) and four from the drains (Fig. 2) were collected using an Ekman grab sampler. The sediment samples were chosen to represent the different sub-basins. For lake Mariut Stations 1, 2 represented the fish farm, stations 3, 4, 5 represented the main basin, stations 6, 7, 10 represent the northwest basin and stations 8, 9 represented southwest basin. For Lake Edku station 9 from the lake sea communication, stations 1, 2, 3, 8 from the western basin, stations 4, 5, 7 from the central basin and station 6 from the eastern basin.

Chemical Analyses and Instrumentation: The samples were analyses according to Folk [25] to determine the mean grain size and the proportions of sand, silt and clay using a standard sieving and pipette techniques. The total organic carbon (TOC) content was determined by oxidation with 1 N $K_2Cr_2O_7$ acidified with concentrated H_2SO_4 and titration with 0.5 N Fe $(NH_4)_2(SO_4)_2$, [26]. Total carbonates and silicate were estimated as described by Molnia [27]. The concentration of total metals were measured using Flame-Atomic Absorption Spectrophotometer (FAAS, Shimadzo 6800, with Autosampler 6100) after complete digestion of sediment samples with mixture of concentrated HNO_3, HF and $HClO_4$ (3:2 :1v/v) according to Origioni and Aston [28]. Total boron concentration was determined by colorimetric Curcumin method as described by Bingham *et al.* [29]. Ca and Mg were determined volumetrically using EDTA standard solution Erio-Chrome T and Murexide indicator [30]. Na, K and Li were measured using a Flame Photometer (JENWAY PEP7).

Statistical Analysis

Enrichment Factor: For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline. The enrichment factors (EFs) for each element were calculated from the formulate [12].

$$EF = (M/Al \text{ or } Li)_{sample}/(M/Al \text{ or } Li)_{crust}$$

According to Zhange and Liu [31] when $0.5 \leq EF \leq 1.5$, trace metals may be entirely from crustal materials or natural weathering processes. However, $EF \geq 1.5$, it suggests anthropogenic source [31].

Factor Analysis/Principal Component Analysis (PCA): Factor analytical technique extracts the eigen values and eigen vectors from co-variance matrix of original variables. The principal components (PC) are the uncorrelated (orthogonal) variables obtained by multiplying original correlated variables with eigen vector, which is a list of coefficients (loading or weightings). Thus, principal components are weighted linear combinations of original variables. PC provides information on the most meaningful parameters, which describe whole data set affording data reduction with minimum loss of original information [32].

RESULTS AND DISCUSSION

Grain Size (Mz): Grain size is the most fundamental property of sediment particles, affecting their entrainment, transport and deposition [33]. Grain size analysis therefore provides important clues to the sediment provenance, transport history and depositional conditions [34, 35].

The parameters used to describe a grain size distribution fall into four principal groups: those measuring (a) the average size, (b) the spread (sorting) of the sizes around the average, (c) the symmetry or preferential spread (skewness) to one side of the average and (d) the degree of concentration of the grains relative to the average (kurtosis).

The mean size in Lake Mariut ranges from 1.12 to 7.22. It was found that, the majority of sediments covering the bottom sediments of main basin (MB), SWB, the sediments in vicinity of El-Max pumping station and El-Nobaria and El-Omom drains rich with silt and clay (Table 1). While the bottom sediments of NWB, station 2 (FB) and El-Kala drain rich with sand fractions. The inclusive graphic standard deviation (σ) ranged from moderately sorted to very poorly sort and the major parts of the Lake Mariut were covered by very poorly sorted sediments. The inclusive graphic skewness (Sk) of the sediments varied between coarse and fine skewed (Table 1). About 30% of the samples are negatively skewed (i.e. coarsely skewed), while 70% of the sediments are positively skewed (i.e. finely skewed). This indicates that Lake Mariut undergoing depositional according to [36]. The inclusive graphic kurtosis (Ku) ranged between platykurtic to very leptokurtic.

The obtained data of grain size revealed that the sediments collected from Lake Edku composed of an admixture of sand silt and clay, having mean grain size varies between 2.9 (station 9) and 6.3 (station 6).

Table 1: Results of grain size analysis, total organic carbon and total carbonate for sediments of Mariut and Edku lakes

Lake	Stations	Mean size	Sorting	Skewness	Kurtosis	Sand %	Silt %	Clay %	Sediment type	TOC%	TCO_3%
Mariut	1	6.1	2.3	-0.19	1.9	11	64	25	fine silt	8.55	41
	2	3.2	2.8	-0.08	1.0	60	34	9	very fine sand	3.39	85
	3	6.7	2.4	0.17	0.9	10	51	39	fine silt	10.02	42
	4	7.2	2.1	-0.14	0.7	6	39	55	very fine silt	2.98	39
	5	7.0	2.1	0.17	0.8	7	50	43	very fine silt	8.82	41
	6	1.1	1.4	0.31	0.8	98	2	0	medium sand	0.98	67
	7	5.7	3.1	0.28	1.4	19	55	26	medium silt	5.16	59
	8	7.2	2.2	-0.17	0.7	7	38	55	very fine silt	1.06	38
	9	6.0	1.9	0.1	1.2	9	66	25	fine silt	4.04	71
	10	3.8	0.9	0.2	1.4	68	31	1	very fine sand	3.22	97
	Average	5.4	2.1	0.065	1.1	29	43	28	medium silt	4.82	58
	El-Kala	0.3	1.1	0.32	1.0	98	2	0	coarse sand	0.06	16
	El- Nubaria	6.3	2.1	0.25	0.9	10	57	33	fine silt	1.26	39
	El-Omom	7.1	2.0	0.03	0.6	4	46	50	very fine silt	2.16	39
	Average	4.6	1.8	0.2	0.9	37	35	28	coarse silt	1.16	31
Edku	1	6	2.3	0.53	1.0	13	58	29	fine silt	3.44	28
	2	3.82	2.5	-0.16	2.0	40	49	11	very fine sand	0.74	27
	3	4.88	2.2	0.39	1.8	37	48	15	coarse silt	1.27	26
	4	3.81	1.3	-0.01	1.7	58	38	4	very fine sand	0.99	37
	5	6.31	2.4	0.41	0.8	13	53	34	fine silt	3.27	56
	6	6.03	2.2	-0.53	1.0	20	36	44	fine silt	2.17	23
	7	5.7	1.6	-0.48	1.2	15	76	9	medium silt	4.35	42
	8	3.1	1.1	-0.29	1.2	84	16	0	very fine sand	0.6	48
	9	2.9	1.0	-0.14	1.1	94	6	0	fine sand	0.54	35
	Average	4.73	1.8	-0.03	1.3	42	42	16	coarse silt	1.93	36
	Bousily	4.03	2.4	0.49	1.7	71	22	7	coarse silt	0.73	17
	Khairy	5.96	3.2	0.33	0.7	36	28	37	medium silt	0.76	20
	Edku	6.38	2.7	0.06	1.3	13	50	37	fine silt	4.66	28
	Barzic	2.89	0.9	-0.18	1.2	100	0	0	fine silt	0.04	14
	Average	4.82	2.3	0.18	1.2	55	25	20	coarse silt	1.55	20

The sand rich sediments prevailed in the lake sea communication, mainly derived from the Mediterranean Sea and marine sediment. Whereas, the eastern basin rich with silt and clay sediments which transported by the drains. The sediment of Barsic and Bousily drains rich with sand fraction while Khairy and Edku drain rich with silt and clay sediments. The sediments for Lake Edku are ranging between poorly and very poorly sorted. This poor sorting of sediments is caused mainly by the crushing of calcareous shells into fragments. Microscopic examination of sands reveals that the sand fraction is entirely of mollusk shells and shell fragments. The skewness of the sediment samples varies between near symmetrical and strongly fine skewed and the major parts of the lake are cover by negatively skewed sediments. The inclusive graphic kurtosis (Ku) ranged between platykurtic to very leptokurtic.

Organic Carbon: 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. The extra-cellular products exudates by the hydrophytes and the precipitated planktonic organisms are expected to be the main autochthonous sources of organic matter in the lake. The distribution of organic carbon in bottom sediments of Lake Mariut shows high concentration (10.02%) recorded at station 3 which affected by industrial influent. Also, station 7 & 5 have high value of organic carbon (5.16 & 8.82 %) respectively that reflecting a high rate of organic matter accumulation from El-Max pumping station and local sewage of the western treatment plant also affected by El-Amria oil drain. The values of organic matter decrease to 0.98% for sediment at station 6 (NWB).The organic carbon reaches to 2.16% for El-Omom sediments.

Apparently, much of the organic matter in Lake Edku is produced in situ. The primary production in the lake was given by [37] as 0.6 gc/m^2/ day for hydrophytes. In addition a terrestrial contribution in the form of organic detritus enters the lake with drainage water. The organic carbon content of Lake Edku varies between 0.54 and 4.35%. In general, the coarser sediments of the lake sea communication and western basin of the lake have low organic carbon content. The finer sediments of the eastern parts are significantly enriched with organic carbon, reflecting high rate of organic matter accumulation. In addition to contribution from local plants and animals, the chance for suspended organic detritus to reach the bottom is great because of the extreme shallowness of this basin. The high organic carbon (3.44%) recorded at station 1 may be attributed to the contribution of plant detritus from the nearby vegetated islets, beside this station affected by the wastes of the fish farm. Also, relatively fine sediments content (mean size 6). For drain sediments the high value 4.66% recorded at Edku drain.

Total Carbonate: The carbonate content of Lake Mariut ranges between 39 and 97%. The major parts of sediments have about 60% of total carbonate. The high carbonate content is due to the contribution of calcareous shells, besides the calcareous sands derived from the limestone ridges.

In the present study, the values of total carbonate for Lake Edku sediments vary from 23 to 56%. The major sources of carbonate in Lake Edku sediments are shells and shell fragments. It is recognized that the biogenic content of lake deposits tends to be higher comparing to their principle sediment source (Nile alluvium) [38]. As well as, carbonate content in sediments from the drains showed average values (31% and 20%) for Mariut and Edku Lake respectively.

Sodium (Na) and Potassium (K): They are alkali metals with the average concentration of 2.1 % by moles for Na and 1.6 % by moles for K in the earth crust. The occurrence of sodium and potassium is related generally to terrigenous origin rather than the marine origin because they are the main cations in the structure lattice of feldspars. Potassium is considered to be non-toxic. Due to its highly reactive nature, elemental potassium must be handled with extreme care. Potassium is vital for plant growth. Plants use it, for example, to make proteins, hence the greatest demand for potassium compounds is in fertilizers. Potassium hydroxide is a strong alkali and an important industrial chemical. It is used in the manufacture of soft soaps and as an electrolyte in alkaline batteries Potassium chloride is used as a healthier alternative to table salt. Potassium does not occur as a free element in nature; it is too reactive, forming compounds from which it is difficult to separate [39].

Both sodium and potassium showed the same pattern of distribution for Lake Mariut surface sediments. The high values (1.13 and 0.32%) for Na and K respectively were recorded at the SW basin which is mostly due to drainage from Omoum drains and El-Amria of petroleum. Lower concentrations are encountered in the in the northwestern basin (station 6) with 0.29 and 0.08%. Jonathan *et al.* [40] concluded that the behavior of Na and K largely reflects the distribution of K and plagioclase feldspars in the sediments.

The distribution pattern of K for the surface sediments in Lake Edku was quite similar to that of Na. The highest value 1.19% and 0.38% for Na and K respectively recorded at station 2. While, the lower value 0.3% and 0.13% recorded at station 7. Generally, the concentrations of Na and K for Edku and Mariut lake drainage sediments were more or less similar to inside the lake sediments.

Calcium (Ca) and Magnesium (Mg): They are alkali metals with the average concentration of 4.2 % and 2.3% by weigh for Ca and Mg respectively, in the earth crust [39]. Calcium occurs in nature in various minerals including limestone (calcium carbonate), gypsum (calcium sulfate) and fluorite (calcium fluoride). Commercially it can be made by the electrolysis of molten calcium chloride, $CaCl_2$. The pure metal can also be produced by replacing the calcium in lime ($CaCO_3$) with aluminum in hot, low pressure retorts. It is one of the most important elements in the aquatic habitats, as it plays an important role in contribution of the abundance of Molluscs, Lamilibranchs, Calcareous warm tubes and other aquatic organisms. Building of shells and skeletons for these organisms continually remove the supply of Ca salts introduced to the lake through drainage waters.

Magnesium is essential in the dolomites and high Mg-calcite and may be present in the amphiboles, pyroxenes. The major host mineral for Mg is likely to be the clays. Moreover, Mg is accumulated in both minerals of detrital and non-detrital origion [41].

The present data depicted that the sediments content of the lake Mariut shows that most of the lake proper eastern side in front of Kalaa drain sewage and industrial wastes, are diluted with sediments relatively lower in Ca and Mg. Where, attainted its minimum values (8.45% and 1.9%) at station 8 for Ca and Mg respectively (Table 2). The sediments of the NW basin are containing high contents of Ca and Mg. Highest extreme concentrations were for station 6 (16.3% and 6. 7%) for Ca and Mg respectively. Jonathan *et al.* [40] attributed the high concentrations of Ca for Gulf of Mannar sediments as they flow through the limestone beds. As well as, Ca and Mg in sediments from the drains showed values (Table 2) lower than those recorded inside the lake.

Table 2: Results of major and trace metals for sediments of Mariut and Edku lakes

Lake	Stations	Na	K	Ca	Mg	B	Li	Co	Bi	Se
Mariut		----------- % -----------				----------- µg/g -----------				
	1	0.45	0.14	10.3	2.7	58.02	76.78	11.63	7.30	4.92
	2	0.83	0.24	15.3	3.7	17.92	74.90	2.32	0.34	1.86
	3	0.45	0.11	12.8	3.2	71.00	88.00	5.92	11.32	0.78
	4	0.44	0.18	10.9	2.4	75.22	81.22	15.91	10.90	0.85
	5	0.35	0.11	12.8	3.3	83.23	75.90	8.01	7.64	0.72
	6	0.29	0.08	16.3	6.7	116.40	154.04	3.89	35.67	0.04
	7	0.43	0.11	14.3	4.7	106.25	80.26	4.79	7.18	0.56
	8	0.90	0.27	8.4	1.9	42.68	309.79	17.19	9.53	0.59
	9	1.13	0.32	11.9	2.4	29.28	73.62	8.67	13.99	0.63
	10	1.02	0.27	13.8	2.8	24.55	68.59	0.63	6.52	0.34
	Average	0.63	0.18	12.7	3.4	62.64	111.81	7.90	11.04	1.13
	El-Kala	0.88	0.24	3.8	1.0	19.96	181.73	3.15	11.18	2.08
	El- Nubaria	0.37	0.13	5.6	1.1	60.97	72.99	16.42	11.43	0.00
	El-Omom	0.39	0.20	5.3	3.1	97.68	75.73	16.81	8.47	0.09
	Average	0.55	0.19	4.9	1.7	59.54	110.15	12.12	10.36	0.72
Edku	1	0.47	0.20	4.9	2.0	33.68	71.41	19.02	5.99	0.63
	2	1.19	0.38	6.7	3.0	21.95	75.73	13.44	11.86	1.39
	3	0.49	0.13	5.2	2.9	26.50	63.02	14.95	5.29	0.67
	4	0.44	0.18	8.6	5.9	59.67	70.54	16.30	13.40	0.85
	5	0.35	0.13	16.8	7.9	51.16	75.03	13.43	6.72	0.66
	6	0.42	0.15	5.8	2.5	46.85	145.94	24.79	6.53	0.12
	7	0.30	0.13	11.0	4.6	66.22	145.69	16.16	10.59	1.06
	8	0.40	0.14	12.4	4.7	28.06	61.00	9.02	8.45	0.91
	9	0.61	0.19	5.7	1.8	29.01	63.04	7.43	11.28	1.28
	Average	0.52	0.18	8.6	3.9	40.34	85.71	14.95	8.90	0.84
	Bousily	0.34	0.16	4.6	2.1	52.84	146.46	25.78	9.01	2.45
	Khairy	0.25	0.19	4.8	0.9	44.26	0.00	15.31	8.71	0.13
	Edku	0.57	0.17	5.8	2.5	30.06	0.00	16.19	5.27	0.79
	Barsic	0.50	0.18	4.3	1.3	11.37	129.10	1.58	7.58	0.55
	Average	0.41	0.18	4.9	1.7	34.63	68.89	14.72	7.64	0.98

The measured concentrations of Ca and Mg in Lake Edku sediment samples were in range 4.9-16.8% and 2.0-7.9% for Ca and Mg respectively, where the lower values recorded at station 1and the highest values recorded in the depth part of the lake (station 5). It is apparent that calcium carbonate and Ca are more abundant on the southern side of Lake Edku where the shell debris is the main constituent. The high Mg content in sediments observed in the southern part indicates that among the different processes, biological processes play an important role. Organisms that secrete carbonate skeletons incorporate varying amounts of Mg into the skeleton. The higher concentration of Mg is may be attributed to Mg^{2+} by the ion exchange process with Ca^{2+} and the skeletal fragments and organisms from the skeletal debris are made up of high Mg-calcite contributing Mg to the present sediments and the dissolution of Mg in the shelf sediments is also available for reprecipitation [42].

Lithium (Li): Pure lithium metal is used in rechargeable lithium ion batteries and the metal is used as an alloy with aluminum, copper, manganese and cadmium to make high performance aircraft parts. It is alkali Metal represents 20 parts per million by weight of the earth crust [43]. Lithium does not occur as a free element in nature. It is found in small amounts in ores from igneous rocks and in salts from mineral springs. Pure lithium metal is produced by electrolysis from a mixture of fused (molten) lithium chloride and potassium chloride. Lithium is an important microelement in underground waters and it is considered by geochemists as being indicative in the determination of the origin of oil field brines [44]. The average concentration for Lake Mariut 111.81 µg/g, the highest score value for Li were found at station 8 (SWB) while the lowest concentration level was recorded at station 10 (NWB) as shown in Table 2. Generally, most sediment Li concentrations were more or less similar to lower concentrations.

Lithium concentration in bottom sediments of Lake Edku varying between 63µg/g and 145 µg/g. The majority of studied sediments has values lesser than 75 µg/g foe Li, the high values restricted the eastern part of lake (Table 2).

Bismuth (Bi): Bismuth is not known to be toxic. It represents 9 parts per billion of earth crust. Commercially, bismuth is produced as a byproduct of refining copper, lead, tin, silver gold and zinc ores. Bismuth compounds account for about half the production of bismuth. They are used in cosmetics, pigments and a few pharmaceuticals, notably Pepto-Bismol. Bismuth has unusually low toxicity for a heavy metal. As the toxicity of lead has become more apparent in recent years, there is an increasing use of bismuth alloys (presently about a third of bismuth production) as a replacement for lead [39]. In general, Bismuth concentrations in most lake sediment and drains sediments of both studied lakes are lower. Bismuth concentration in Lake Mariut fluctuates between 0.34 µg/g at station 2 and 35.67 µg/g at station 6 (NW basin). For sediments of Lake Edku the higher concentration 13.4 µg/g recorded in station 4 which affected by drainage water from Barsik drain water. While lower value 6.5 µg/g recorded at station 1 of the western part.

Cobalt (Co): Cobalt is a naturally occurring element found in rocks, soil, water, plants and animals, it is used to produce alloys used in the manufacture of aircraft engies, magnets, grinding and cutting tools, artificial hip and knee joints. Cobalt compounds are also used to color glass, ceramics and paints and used as a drier for porcelain enamel and paints Cobalt in small amounts is essential to many living organisms. Human toxicity due to Co exposure is uncommon and in general, Co is beneficial to humans because it is part of vitamin B_{12}, which is essential for humans [45]. It represents 25 parts per million of earth crust.

Lake Mariut recorded concentration levels of cobalt fluctuated between 0.63 µg/g at station 10 to 17.19 µg/g at station 8 (SW basin) which affected by Omoum drains. It was found that the majority of sediments covering the bottom inside the lake lower than recorded for drain sediment with average value 7.90 and 12.12 µg/g, respectively.

Lake Edku recorded that the sediment content of Co inside the lake and drain sediment attained more or less similar value (average 14.95 & 14.72 µg/g), respectively. The range of Co level in the studied sediment for Lake Edku was 7.43-24.79 µg/g with the lowest value at station 9 and the highest at station 6are due to the effect of drain water discharged to the lake. The variation of the concentration of cobalt depends on the structure of sediment and clay. In general, the coarse sediments had low cobalt content, while, the finer sediment of the lakes and drains were significantly enriched with Co. The USEPA established a cleanup level of 80 µg/g for Co in stream sediment in the Blackbird area [46]. Thus the investigated sediments are considered unpolluted by Co. The concentration of Co in the present study was relatively lower than that recorded by Karadede-Akin and Űnlű (17.3 ± 0.76 µg/g) for sediment collected from Tigris River, Turkey [47] and (26.265 ± 7.514 µg/g) for sediment along the Mediterranean Egyptian coast [48].

Boron (B): Boron is an essential micronutrient for plants and animals and is vital for human health [49]. However, B contamination in soils, sediments and water can cause health problems, mainly from food sources, but high boron solubility can also affect drinking water [50]. Contamination can also influence the agro-industrial economy, as it can be toxic for crop plants, thus reducing yields (e.g., 17% yield reduction in barley crops [51].

Boron can be found in the form of boric acid or its salt (borate) in soils, sediments and groundwater as a consequence of its natural presence in many silicate minerals; however, only borax, colemanite, kernite and uxelite are mined extensively [52]. Areas with a history of volcanism and geothermal ducts frequently have boron-containing minerals [53]. Boron can also be released in the environment from anthropogenic activities: e.g., the use of borate-containing fertilizers, herbicides and detergents, glass and ceramic production, release of waste from borate mining processing [52], etc.). It represents 10 parts per million of earth crust. Goldberg [54] Concluded that natural weathering of clay-rich sedimentary rocks on land surface accounts for a large proportion of boron mobilized into soils and the aquatic environment, amounting to 360,000 tons of boron annually.

In Lake Mariut the boron concentration ranged from a minimum of 17.92µg/g at station 2 (FB) to a maximum of 116.4 µg/g at station 6 (NWB) may be due to the effect of El-Amria Drain.

For Lake Edku boron concentrations fluctuated between 21.95µg/g and 66.22 µg/g, the high recorded values at the eastern part of the lake may be due to the effect of waste water discharged from the drains at the eastern side of the lake. The lowest boron contents were perhaps due to the type of sediment and the relative amount of organic carbon. Faragalla *et al.* [55] conclude that available boron is controlled by physical and chemical properties of the sediment, such as pH, grain size, clay minerals, organic matter, etc. The concentration of B in the present study was relatively lower than that reported by Xu *et al.* [56] for sediment collected from Abu-Qir Bay (192.06 ±51.11 µg/g) and from El-Max Bay (182.59±48.21 µg/g).

Selenium (Se): Selenium may be enriched in agricultural soils due to human activities such as mining, waste irrigation, coal burning and selenium fertilizer application [57]. Selenium is presented relatively rare in the earth crust with the average concentration of 50 parts per billion by weight, 10 parts per billion by moles. Bottom sediments are the dominant sink for Se in aquatic ecosystems via association with suspended particulate matter and subsequent deposition [58]. The sediment component of aquatic ecosystems is an important pathway of selenium movement through the food web.

In this study the concentrations of Se in Lake Mariut were within the range 0.04 to 4.92 µg/g with the lowest value at station 6 and the highest value at station 1(fish basin), which was above the value recorded by Woock [59] as (0.5 µg/g) to represent the threshold between uncontaminated, background conditions and environments with elevated selenium concentrations. Se tends to sorb most rapidly to fine-rather than coarse-textured substrate [58], consistent with greater surface area for Se sorption and the elevated Se concentrations in some lentic area sediments.

The maximum concentration of Se in surface sediments of Lake Edku was 1.39 µg/g, at station 2 near the cages of fish farms. While, the lower concentration 0.12 µg/g recorded at station 6. Chen *et al.* [60] demonstrated in a cage study with golden shiner (*Notemigonus crysoleucas*) that fish in cages with access to bottom sediments (sediment, benthic invertebrates and detritus) accumulated more selenium than fish held in cages suspended about 1.5 m above the sediments. The selenium concentrations are higher in the lake sea communication 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.

Enrichment Factor (EF): Enrichment factor is good tool to differentiate the metal source between anthropogenic and naturally occurring [61]. Li, Cs, Sc, Fe and Al have been utilized as reference elements [62]. In this study Lithium was used as a reference element.

The calculated EF values Figure (4) for all surface sediments for both two lakes revealed that all stations in the present study have Co, Bi, Na, K and Ca are generally less than 1.5 (EF ‹ 1.5), suggesting lithogenic origin. The combination of normalization techniques confirms that B for most Station for Lake Edku (EF range 0.58 and 1.69) are mainly of natural origin, with the exception of some local anomalies. These anomalies are directly associated with point discharges from municipal, dock and industrial activities.

For Lake Mariut EF (B) ranges from 0.27 and 2.65, this indicated that there were other natural or anthropogenic sources in addition to weathering. Finally, the results of normalization routines showed that all stations with the highest degree of enrichment (greater than 1.5) for Se in the different two lakes except station 6 and 8 for Lake Mariut and station 6 for Lake Edku exhibited lower EF. The reason behind these elevated values might be man's activities (municipal discharges, industrial development, agricultural drainage, Fish farms…..etc.

Factor Analysis/Principal Component Analysis (PCA): In Lake Edku the distribution manner of individual association of elements was determined by Principal Rotated Varimax Factor analysis (Table 3) which was applied on (TCO_3, TOC, Ca, Mg, K, Na, Li, B, Bi, CO and Se). Four factors explaining 82.32% of total variance adopted for these parameters in sediments. Large absolute values > 0.70 (indicating a reliable correlation). PC1; explained (28.62%) had a high positive factor loading for Ca (0.958), Mg (0.936) and TOC (0.969). It revealed the strong association among TCO_3, Ca and Mg. PC2; explained (20.2%) had high positive factor loading to Na (0.942) and K (0.928). Since, high sodium contents in marine sediment attributed to lithogenic origin revealing the ability of certain organisms to concentrate sodium [62] PC2 pointed to the geochemical cycle of K and Na related to each other. PC3 (17.16%) possessed positive loading to Bi (0.721) and Se (0.713). Lake Edku may be received industrial, agricultural and farm wastewater included Bi and Se. Selenium had low concentrations, it strongly affected the variance in sediments composition. PC4; yields high loading for Co (0.885) and TOC (0.724) pointed to strong association of Co with total organic carbon due to formation of different complex structures among Co and many organic ligands [63]. 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 [16]. In addition to industrial and agricultural activities along the eastern parts of the lake.

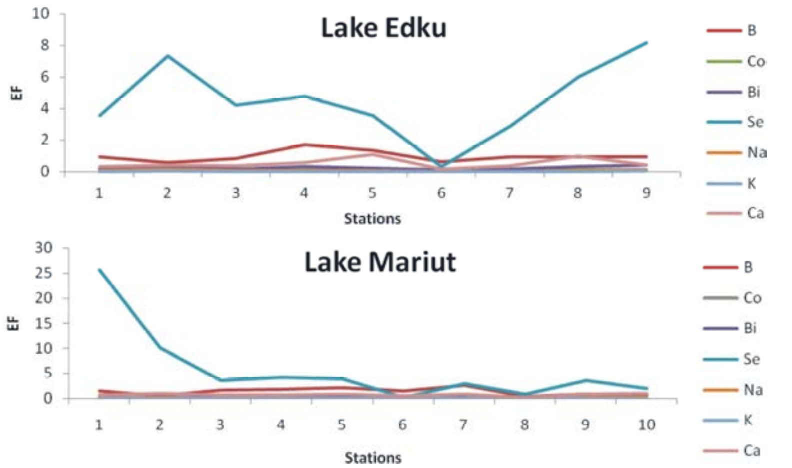

Fig. 4: The mean enrichment factor (EF Li) for metals in surface sediments from Mariut and Edku Lakes

Table 3: Varimax normalization rotated factor loadings in sediments of Lake Edku

Parameter	PC1	PC2	PC3	PC4
Na	-0.086	0.942	0.044	-0.152
K	-0.191	0.928	0.143	-0.087
Ca	0.958	-0.140	-0.009	0.001
Mg	0.936	-0.091	0.099	0.111
Boron	0.402	-0.396	0.417	0.604
Li	-0.086	-0.293	0.646	0.121
CO	-0.179	-0.119	0.221	0.885
Bi	0.254	0.339	0.721	-0.227
Se	-0.031	0.255	0.713	0.129
TOC	0.324	-0.062	-0.427	0.724
TCO_3	0.969	-0.060	-0.064	0.003
Variance %	28.620	20.200	17.160	16.340
CV%	28.620	48.820	65.980	82.320

Extraction Method: Principal Component analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 6 iterations, N =13. CV: cumulative variance; bold numbers indicate positive correlation and –ve italic values indicate negative correlation.

Table 4: Varimax normalization rotated factor loadings in sediments of Lake Mariut

Parameter	PC1	PC2	PC3	PC4
Na	-0.955	0.169	0.133	-0.020
K	-0.932	-0.053	0.090	-0.173
Ca	0.188	0.910	-0.146	0.009
Mg	0.570	0.747	0.145	-0.134
B	0.934	0.031	0.028	-0.242
Li	-0.185	-0.220	0.848	0.046
Co	0.182	*-0.802*	-0.018	-0.207
Bi	0.471	0.259	0.646	-0.272
Se	-0.115	-0.052	-0.052	0.909
TOC	0.324	0.193	-0.573	0.556
TCO_3	-0.309	0.815	-0.252	-0.299
Variance %	31.970	26.200	14.560	13.190
CV%	31.970	58.170	72.730	85.920

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Rotation converged in 6 iterations, N =13.

In Lake Mariut (Table 4) PC1, PC2, PC3 and PC4 represented 85.92% of total variance adopted for TCO_3, TOC, Ca, Mg, K, Na, Li, B, Bi, CO and Se in sediment. PC1; explained 31.97% positive loading with Boron (0.934) and negative loading to Na (-0.955) and K (-0.932). PC1 assigned that the geochemistry of Lake Mariut highly affected by Boron distribution and inverse relationship existed between (Na, K) and Boron. PC2; represented 26.2%had positive loading to Ca (0.910), Mg (0.747) and TCO_3 (0.815) and negative loading to Co (-0.802). From PC2, it could be concluded that the geochemistry of the sediment in lake Mariut controlled by the concentration of TCO_3, Ca and Mg.PC3; represented 14.56% had positive loading to Li, which indicated that this elements was important constituents of one or more of the major fine-grained trace metal carrier (s) and reflect a granular variability in the sediments [26] and lithogenic in origin. PC4; represented 13.19% had positive loading to Se (0.909).

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