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Some heavy metal contents in surface water and sediment as a pollution index of El-Manzala Lake, Egypt

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Abstract:

El-Manzala Lake is one of most important lake in north Delta of Egypt. It is exposed to huge amounts of serious pollutants especially heavy metals. The main objective of this research was to evaluate the spatial distribution of the heavy metals in water and sediment of the lake. Accordingly, Metal index (MI) and pollution index (PI) were calculated to assess the contaminations of the lake water with the metals named Fe^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2}. MI and PI values confirm that most sites of aquatic utilizations are highly polluted with the mentioned metals. Four Pollution Indices were used for the environmental assessment of Lake sediment. The indices included three single indices, Enrichment Factor (EF), Index of Geo-accumulation (Igeo) and Contamination Factor (CF). While the fourth, Pollution Load Index (PLI) was an integrated index. The pollution indexes confirmed that the Lake sediment was contaminated with these elements. This is attributed to discharging of the effluents of different industrial wastes into the lake.

Key words: El-Manzalah Lake, Heavy metals, pollution index

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1. Introduction:

In recent years, the aquatic environment and related issues have been a major concern of the public because most of our ecological water systems are being continuously contaminated [**1**].The existence of excess heavy metals in the aquatic environment especially lakes and rivers constitutes a threat to humans because of their toxicity and of the potential pollution to the food chain. As a result, increasingly stringent restrictions are being imposed on the release of these compounds by various regulatory bodies [**2**].

In natural aquatic ecosystems, metals occur in low concentrations, normally at the nanogram to microgram per liter level. In recent times, the occurrence of metal contaminants especially the heavy metals in excess of natural loads has become a problem of increasing concern. This situation has arisen as a result of the rapid growth of population, increased urbanization, expansion of industrial activities, exploration and exploitation of natural resources, extension of irrigation and other modern agricultural practices as well as the lack of environmental regulations [**3**].

Heavy metals are natural trace components of the aquatic environment, generally enter the aquatic environment through atmospheric deposition, erosion of the geological matrix, or due to anthropogenic activities but their levels have increased due to industrial effluents, domestic sewage, and mining [**4**]. Heavy metals have a higher tendency to be incorporated into food chains and become accumulated in tissues and organs of fish and other aquatic organisms and this represent serious health hazards to consumers. Fishes are more liable to be affected with environmental pollutants than the land animals and can accumulate heavy metals from their environment and act as indicators for these elements in the environment [**5**].

El-Manzala Lake is one of the most polluted lakes in Egypt. The sediments act as "sink" for metal contaminants, and risk increases with increasing metals leachability. The impact of such heavy metals abnormality may extend to involve the water quality and food web, and hence to the human health. In the studied area, sources of the toxic metals could be natural or anthropogenic. This is contributed by industrial, domestic, human activities, sewage and huge amounts of agriculture brackish water wastes from drainage system at all direction. The most widely recognized issue is that of agricultural drains as Hados, Bahr El-Baqar and Ramses drains which open into the southern beach of the lake [**6**].

The main objective of this study is mainly to assess the distribution pattern of the lake heavy metals according the international constrains imposed by the Egyptian standards and the world-wide organizations. Increasing awareness of pollution risk may support the implemented mitigation and remediation programs to face the rapid deterioration of this important aquatic ecosystem.

2. Materials and Methods

2.1. Study area description.

Manzala lake is the largest Egyptian coastal lake, it lies on the eastern north coast of Egypt. Figure1 shows the layout of the lake, its dimensions are about 47 Km long and 30 Km wide. This lake serves five provinces of Nile Delta (Damietta, Dakahliya, Sharkiya, Ismailia and Port Said). Economically, Manzala Lake is considered as one of the most valuable fish sources in Egypt, it contributed about 35% of the total country yield during 1980's [**7**]. In the present, it is considered as the most productive lake in Egypt and contributed by about 30% from the total annual production of the Egyptian lakes, which contribute by about 12.5% of Egypt total fish production [**2**]. The northern boundary of the lake is the Mediterranean Sea (there are some narrow outlets, the main outlets are El-Gamil outlet and the New El-Gamil Outlet), while the eastern boundary is Suez Canal (there is a very narrow connected canal called El- Qabuty Canal). Damietta Branch of River Nile is considered its western boundary (the lake is connected to Damietta Branch by Enanya Canal). The lake receives the discharges of a lot of drains, such as Fareskour, Elserw, Mataria, Hadous, Ramsis and Bahr Elbaqar which are considered the main drains (according to their discharges). The drained waters can be classified as an agricultural, industrial and domestic waste. Water fluctuated from low salinity in the south and west to brackish water over the most of its area to saline water in the extreme northwest. The lake hydrological and water quality status have been degraded due to the progressive increasing of industrial and agricultural waste water discharge [**8**].

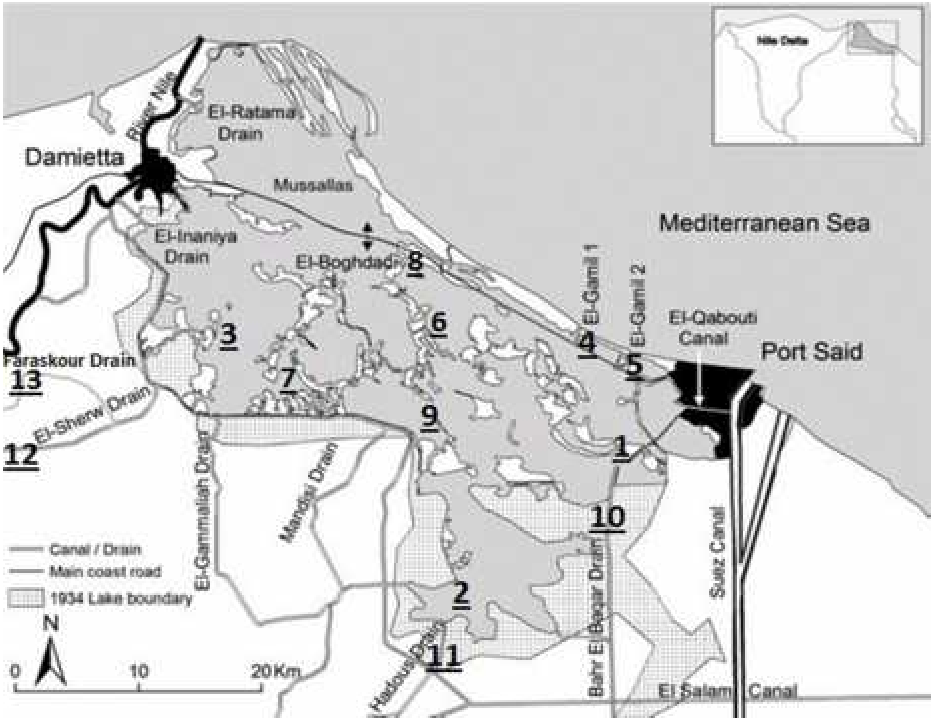

Fig (1): The sample locations at El-Manzala Lake [9]

Table 1: Stations details of area under investigation

Station	Features of station	Latitude	Longitude
S1	In front of Bahr El Baqar drain	$31^{o}\ 11^{\backslash}\ 51^{\backslash\backslash}$	$31^{o}\ 15^{\backslash}\ 10^{\backslash\backslash}$
S2	In front of Hadous drain	$30^{o}\ 06^{\backslash}\ 41^{\backslash\backslash}$	$31^{o}\ 16^{\backslash}\ 22^{\backslash\backslash}$
S3	In front of El serw drain	$31^{o}\ 16^{\backslash}\ 44^{\backslash\backslash}$	$31°49^{\backslash}\ 16^{\backslash\backslash}$
S4	EL Gmail 1	$31^{o}\ 15^{\backslash}\ 32^{\backslash\backslash}$	$32^{o}\ 12^{\backslash}\ 12^{\backslash\backslash}$
S5	EL Gmail 2	$31°13^{\backslash}\ 33^{\backslash\backslash}$	$32°06^{\backslash}\ 24^{\backslash\backslash}$
S6	Legan station	$31°14^{\backslash}\ 26^{\backslash\backslash}$	$32°\ 00^{\backslash}15^{\backslash\backslash}$
S7	Digdi station	$31°13'26^{\backslash\backslash}$	$32°02^{\backslash}\ 43^{\backslash\backslash}$
S8	EL Hamra station	$31^{o}\ 16^{\backslash}\ 35^{\backslash\backslash}$	$32^{o}\ 06^{\backslash}\ 37^{\backslash\backslash}$
S9	Mataria station	$31^{o}\ 11^{\backslash}\ 55^{\backslash\backslash}$	$32^{o}\ 02^{\backslash}\ 21^{\backslash\backslash}$
Dr 1	Bahr El-Baqar drain	$31^{o}\ 11^{\backslash}\ 51^{\backslash\backslash}$	$32^{o}\ 12^{\backslash}\ 18^{\backslash\backslash}$
Dr 2	El Hadous drain	$31^{o}\ 06^{\backslash}\ 19^{\backslash\backslash}$	$32^{o}\ 00^{\backslash}\ 17^{\backslash\backslash}$
Dr 3	El serw drain	$31^{o}\ 15^{\backslash}\ 21^{\backslash\backslash}$	$31^{o}\ 48^{\backslash}\ 45^{\backslash\backslash}$
Dr 4	Farskour drain	$31^{o}\ 15^{\backslash}\ 23^{\backslash\backslash}$	$31^{o}\ 48^{\backslash}\ 39^{\backslash\backslash}$

2-2.Pollution Resources

The following are the main drains with their relative contribution of the total flow in water that discharge to the lake and considered as a source of different pollutants

- Bahr El-Baqar: Serves an agricultural area of about 119.2 km^2, and receives about 300 million m^3/year of treated and untreated sewage from Cairo (25% of total inflow).
- Hadous: Is the largest drain in the eastern delta, serving some of agricultural land of about 1756.96 km^2 (49 %).
- ElSerw: Agriculture drain, serves 68,700 feddans (152.8 km^2), 13% of total inflow.
- Faraskur: Agricultural drain, serves 20,000 feddans, an area of about 44.48 km^2 (4% of total inflow).
- Ramsis: Discharges a relatively small amount of water to Manzala Lake (24 km^2).
- Matariya: It serves 50,000 of land under agricultural reclamation (2%) [**10**].

2-3.Samples collection

Nine surface water and sediment samples; from the lake and four from the selected drains; were collected during summer 2015 and winter 2016. Water samples were collected from a depth 40 cm (one sample from each) using automated water sampler (21 cc capacity). Samples for heavy metal analysis were stored in amber-colored polyethylene bottles (1 L) prewashed with 1 (N) HNO_3 and deionized water. To prevent further oxidation or any fungal growth, 5mL concentrated HNO_3 was added. Nine surface sediment samples were collected from the same locations, which were quickly packed in air tight polythene bags. Then, subsamples of the sediments were oven dried at $105^{o}C$ to constant weight and were grinded using mortar and pestle.

2.4. Samples analysis

2.4.1. Water analysis

Water temperature, electrical conductivity and pH value were measured in situ, using Hydrolab, Model (Multi Set 430iWTW). The transparency was measured using Secchi-disk (diameter 30 cm). Water temperature (°C), pH and conductivity (mScm/1) were in-situ measured using Hydrolab model (Multi Set 430iWTW), after previous calibration [11]. Dissolved oxygen (mg L^{-1}) was carried out using modified Winkler method. Total Fe^{+2}, Mn^{+2}, Zn^{+2} Cu^{+2}, Pb^{+2} and Cd^{+2} were measured after digestion by conc. HNO_3 using an atomic absorption reader (Savant AA AAS with GF 5000 Graphite Furnace).

2.4.2. Sediment analysis

Complete digestion of sediment was done according to reference **12**. Equal amounts (15 ml) of concentrated nitric acid, hydrofluoric acid and perchloric acid were added to 0.5 gm of the finely ground sediment material into Teflon beaker. Teflon beakers were covered and set aside for several hours, then evaporated to few drops. The 5 ml of $HClO_4$ were added again and evaporated just to dryness. 10 ml of concentrated HCl were added and the beakers were placed back on a hot plate until the solution was clear and the fumes ceased. Deionized distilled water were added and the digested material was filtered, then the residue washed several times with deionized distilled water and complete to 100 ml volumetric flask. Fe, Mn, Zn, Cu, Pb and Cd were analyzed as the water samples.

2.4.3. Statistical analysis

Data were analyzed for spatial and temporal variations through Excel-Stat software using Multivariate Analysis; significance levels of tests were taken as $p<0.05$ and highly significant as $p< 0.01$. The correlation coefficient (r) between the measured parameters was examined.

2.5. Pollution index

For Water samples two pollution indices, Pollution index (PI) **[13]** and Metal index (MI) **[14]** are used to assess the heavy metal level in water of El-manzala lake. On the other side, four pollution indices were used for the environmental assessment of the sediment. The indices included three single indices: Enrichment Factor (EF), Index of Geo-accumulation (Igeo), and Contamination Factor (CF), while the fourth; Pollution Load Index (PLI); is integrated indices **[15].**

3. Results and Discussion

3.1. Physico-chemical characteristics

Temperature plays an important role in aquatic ecosystem health and affects the speed of chemical reactions, the metabolic rate of organisms, as well as how pollutants, parasites and other pathogens interact with aquatic residents [16]. The values of water temperature varied in the ranges of 25.00-26.90 and 12.40-14.00°C during summer and winter, respectively (Table 2). ANOVA results show a highly temporal significant difference ($p< 0.01$). This is attributed to that the water temperature followed, to a great extent, the corresponding air temperatures. The water temperature of the lake depends mainly on the climatic conditions, sampling times, the number of sunshine hours and also affected by specific characteristics of water environment such as turbidity, wind force, plant cover and moisture **[17]**. Temperature is negatively correlated ($n=18$, $p< 0.05$).

Water transparency determines the depth of the photic zone and consequently affects the lower limit of light penetration that influences the primary productivity of a lake. Plankton also reduces transparency in natural waters [**18**]. The values of water transparency were found in the ranges of 10-40 and 30-60 cm during summer and winter, respectively (Table 2), with a high temporal significant difference ($p< 0.01$). In the drains, it down to (5 cm) at Bahr El-Baqar drain. The low transparency values at all stations indicated the turbidity of the lake water due to the huge amounts of different wastes that discharching into the lake. The remarkable decrease in transparency values was recorded at the discharging point of Bahr El Baqar drain. The present results are in agreement with **[19].**

Conductivity can be measured to establish a pollution zone, around an effluent discharge, or the extent of influence of run-off waters **[20]**. The increase of electrical conductivity values is due to the elevation of total dissolved solids **[21]** as well as the presence of domestic and agricultural wastes containing high amount of inorganic and organic constituents **[22]**. EC showed a highly spatial significant difference ($p < 0.01$). EC is positively correlated ($n=18$, $p< 0.01$) with salinity. Results reveal that the maximum value (40700 μmhos/cm) was recorded at station (5) in winter season due to periodic intrusion of Sea Water through El-Gamil outlets. On the other hand, the minimum value (1830 μmhos/cm) was recorded at station (3) during winter. For drains, the maximum value of EC (3610 μmhos/cm) and the minimum value (1020 μmhos/cm) were recorded at Bahr El-Baqar drain and Faraskour drain in winter season, respectively.

The salinity in the lake varies greatly. It is low near the drain and canals outflows in the south and west and it is high in the extreme north due to El Gamiel outlets. Brackish conditions predominate over much of the remainder of the lake.The maximum value of 25.22 % was recorded at station 5 during winter, while the minimum value of 1.17 ‰ was recorded at station (7) during summer. For the drains, salinity fluctuated between 0.70-2.01 ‰.

The pH is an important variable in water quality assessment as it influences many biological and chemical processes within a water body and all processes associated with water supply and treatment. pH values were varied in the ranges of 7.28-8.95 and 7.95-8.59 during summer and winter, respectively. ANOVA results showed that pH has spatial significant difference between the stations. The results showed that pH values tend to the alkaline side. That may be due to the increased photosynthetic activity of planktonic algae, or to the chemical nature of water **[23-24]** The pH values of the drains water ranged between **7.22-8.04 mg/l.** The relative increase of pH values in summer may be attributed to the photosynthesis and growth of aquatic plants, where photosynthesis consumes CO_2 leading to arise pH values **[25]**. This result agreed with that reported by **[26]**, who revealed that pH elevation was due to the dense of vegetation and phytoplankton, which were accompanied by photosynthetic activities and consumption of CO_2. While the relative decrease in pH values during cold seasons (winter) may be attributed to the increase the solubility of carbon dioxide (due to the decrease of water temperature) and hence increase the bicarbonate ions.

Dissolved oxygen is considered as an important parameter in assessment of the degree of pollution in natural water **[27]**. DO content indicates the health and ability of the water body to purify itself through biochemical processes **[28].** Dissolved Oxygen varied between 0.39-8.86 and 0.81-12.16 mg/l during summer and winter, respectively with noticeable spatial significant differences. It is north that the lowest value of 0.39 mg/l was recorded at station 1 (in front the discharging point of Bahr El Baqar drain), while the highest one was recorded to be 12.16 mg/l at station 4 (in front El Gamil 1 outlet). The corresponding values in the drains changed between complete depletion and 2.65 mg/l. The negative correlation between DO/Cu ($r= -0.49$ at $p<0.05$, $n=18$), and DO/ Mn ($r= -0.69$ at $p<0.01$, $n=18$), indicates the important role of dissolved oxygen in the precipitation of metals as metal oxides and hydroxides **[29].**

Table 2: Some physico-chemical characteristics of El Manzala lake water during 2015-2016

site	Temp. °c		Trans. cm		EC ms/cm		S ‰		pH		DO mg/l	
	S	W	S	W	S	W	S	W	S	W	S	W
S1	25.9	14.0	10.0	30.0	4.14	4.01	2.61	2.75	7.28	7.95	0.39	0.81
S2	26.8	13.1	25.0	60.0	3.38	3.09	2.13	2.12	7.89	8.14	5.99	7.36
S3	26.0	13.4	25.0	40.0	2.25	1.83	1.25	1.51	7.54	8.21	7.64	8.42
S4	26.0	12.9	35.0	30.0	38.8	34.0	22.1	23.4	8.95	8.53	8.57	12.1
S5	25.0	13.0	25.0	30.0	40.7	37.2	24.8	25.2	8.74	8.59	7.73	11.6
S6	26.0	13.8	30.0	55.0	3.78	4.70	2.58	2.55	8.26	8.21	8.36	9.00
S7	26.1	12.4	30.0	60.0	3.23	2.17	1.17	2.16	8.36	8.32	7.63	7.11
S8	26.1	13.1	40.0	50.0	12.1	11.0	6.98	6.94	8.25	8.15	8.86	8.84
S9	26.9	13.8	20.0	30.0	2.83	2.18	1.44	1.81	7.85	8.08	6.54	5.40
Dr 1	26.4	14.6	5.00	20.0	3.20	3.61	2.39	2.01	7.22	7.92	0.20	0.00
Dr 2	24.0	14.7	40.0	40.0	2.22	3.78	2.51	1.55	7.56	7.97	1.88	2.65
Dr 3	25.6	14.3	30.0	40.0	1.51	1.04	0.73	1.09	7.47	8.04	1.90	2.39
Dr 4	24.9	14.6	20.0	35.0	1.51	1.02	0.70	1.02	7.46	7.94	2.39	1.90

S: Summer; W: Winter

3.2. Heavy Metals

Studies on heavy metals in rivers, lakes, fish and sediments have been a major environmental focus especially in the last decades **[30].** Water pollution by trace metal ions is one of our most serious environmental problems. Effluents resulting from daily domestic and industrial discharging may induce serious changes in the physical and chemical properties of El Manzala lake. Heavy metals are regard as serious pollution of aquatic ecosystem because of their environmental persistence and toxicity effects on living organisms [31]. In the aquatic environment, the trace elements are partitioned among various environmental components (water, suspended solids, sediments and biota) **[32].**

The values of iron varied in wide ranges 216.74-736.28 and 251.96-862.36 µg/l during summer and winter, respectively. Iron showed highly spatial significant differences. The iron concentrations in drains were found in the ranges of 819.62-1816.36 µg/l while the maximum value (1816.36 µg/l) was recorded at Bahr El-Baqar drain in winter and the minimum value (819.62 µg/l) was recorded at Faraskour drain in winter. The obtained results declared that, iron concentrations fluctuated in wide ranges during the studied period. The trend of the distribution pattern was mainly attributed to the effect of domestic and agricultural wastes discharged into the lake. The highest levels of heavy metals were found during winter, while the lowest values occurred during summer. The present results showed that the highest value of iron concentrations (862.36 µg/l) recorded during winter at station (1) may be attributed to the sea water effluents which loaded with high concentrations of iron. At the same time, the lowest value of iron (216.74 µg/l) recorded during summer at station (5) may be due to its adsorption on the large amounts of organic matter and also to the high concentrations of dissolved oxygen leading to oxidation of iron from Fe to Fe^{3+} according to the following equation **[33].**

The variations of manganese concentrations were recorded in Table (2) and represented graphically in Figure (2). The values of manganese varied in the ranges of 8.65-26.19 and 11.29-34.62 µg/l during summer and winter, respectively. Manganese values showed a highly spatial significant difference ($p< 0.01$). The manganese concentrations in drains were found in the ranges of 21.65-43.16 µg/l while the maximum value (43.16 µg/l) was recorded at Bahr El-Baqar drain in winter and the minimum value (21.65 µg/l) was recorded at Faraskour drain in summer. The minimum value of Mn (8.65 µg/l) was recorded at station (5) during summer and the maximum one (34.62 µg/l) was recorded at station (1) during winter, which may be due to the agricultural, domestic sewage effluents and the effluents of the drain.

The values of zinc varied in the range of 22.18-56.25and 26.32-58.35 µg/l during summer and winter, respectively. There is a highly spatial significant difference for zinc ($p< 0.01$). The zinc concentrations in drains were found in the ranges of 48.62-149.22 µg/l while the maximum value (149.22 µg/l) was recorded at Bahr El-Baqar drain in winter and the minimum value (48.62 µg/l) was recorded at Faraskour drain in winter. The present results showed that, the lowest value of zinc (22.18 µg/l) recorded during summer at station (5) may be due to its adsorption on precipitated $Fe(OH)_3$ **[34].** While the highest value (58.35µg/l) recorded during winter at station (1) may be due to domestic effluents from drains to the lake.

Average copper abundance in earth's crust is 68 ppm; in soils it is between 9 and 33 ppm Copper is a micro nutrient fundamental to all forms of life; it may be toxic to organisms by inducing a reduction in enzyme activity or a random rearrangement of structural proteins **[35].** The variations of copper concentrations were cited in Table (2) and represented graphically in Figure (2).The values of copper varied in the ranges of 4.25-14.29 and 4.78-14.95 µg/l during summer and winter, respectively. Copper values showed a highly spatial significant difference between stations ($p<0.01$). The copper concentrations in drains were found in the ranges of 10.05-18.25 µg/l while the maximum value (18.25 µg/l) was recorded at Bahr El-Baqar drain in summer and the minimum value (10.05 µg/l) was recorded at Faraskour drain in winter. The highest value (14.95 µg/l) recorded at station (9) during winter season may be due to the agricultural runoff and domestic sewage effluents where domestic sources are the major contributors of copper in the environment. The lowest value (4.25 µg/l) was recorded at station (4) during summer season.

The highest value of lead (74.66 µg/l) recorded at station (1) during winter season may be attributed to the heavy agricultural run-off which contains fertilizers, agrochemicals and pesticides **[36].** While the lowest value (7.95 µg/l) recorded at station (5) during summer season may be due to the uptake of Pb by phytoplankton and zooplankton, fish and other aquatic organisms in surface water. The concentration of lead in water like that of other metals, is affected by pH, hardness, organic matter, presence of other metals **[29],** and is limited by its solubility i.e. it is present in $PbSO_4$ form, it is much soluble than carbonate form, while PbS has very low solubility **[37].**

The values of Cadmium were varied in the lake sediment in the ranges of 0.98-3.18 and 1.04- 3.68 (µg/l) during summer and winter respectively. The maximum value 3.68 µg/g was recorded at station (3) in winter. This may be attributed to the discharge effluents from drains, while the minimum value 0.98 µg/l was recorded at station (5). The cadmium concentrations in drains were found in the ranges of 6.35-11.76 µg/l while the maximum value (11.76 µg/l) was recorded at Bahr El-Baqar drain in winter and the minimum value (6.35 µg/l) was recorded at Faraskour drain in winter.

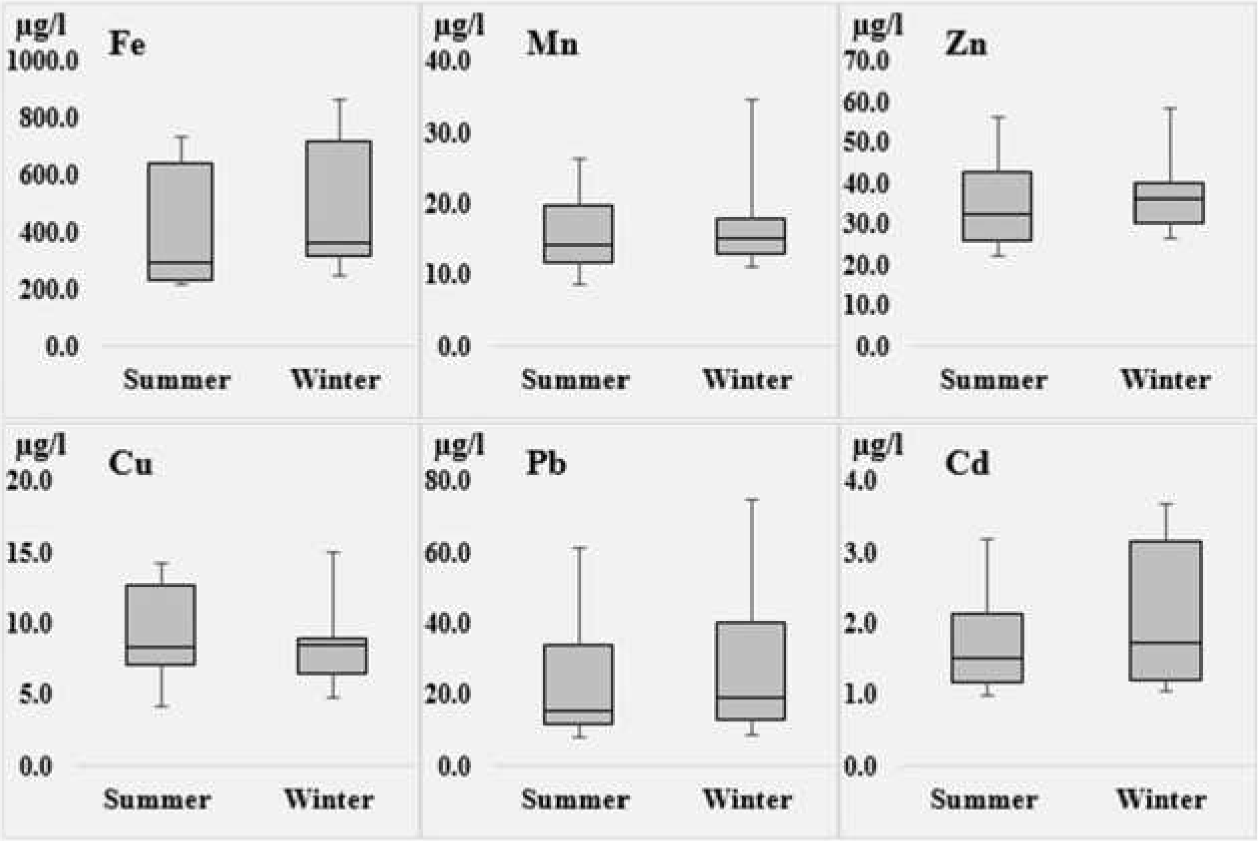

Fig (2): Multiple box and whisker plots of measured heavy metals concentrations in El-Manzala Lake water during 2015-2016

3.2-A. Metal quality indices

3.2-A.1. Pollution Index (PI)

Six metals (Fe, Mn, Cu, Zn, Pb, and Cd) are selected to assess the metal pollution of El-Manzala lake water according to the pollution index. El-Manzala lake water suffers from obviously different contamination grades with the measured metals for different utilizations. Mn exhibits a slightly pollution effect at various locations according to the aquatic life criteria. Fe and Pb show a strongly pollution effects at the most studied sites for aquatic life utilizations. Zn, Cd and Cu recorded no pollution effects at all stations along the canal as shown in Table (3).

Table (3) Pollution index of the measured metals in El-Manzala lake water according to guideline levels of aquatic life utilizations.

statio	Fe^{2+}	effect	Mn^{2+}	effe	Zn^{2+}	effect	Cu^{2+}	effect	Pb^{2+}	effect	Cd^{2+}	effect
S1	3.	strongly	0.0	no	1.1	slight	3.1	strongly	5.	serious	3.2	strongl
S2	2.	moderate	0.0	no	0.8	no	1.1	slightly	0.	no	4.0	strongl
S3	2.	moderate	0.0	no	1.0	slight	1.3	slightly	3.	strongl	5.1	serious
S4	3.	strongly	0.0	no	0.7	no	3.1	strongly	0.	no	3.7	strongl
S5	3.	strongly	0.0	no	0.6	no	2.4	moderate	0.	no	4.6	strongl
S6	2.	moderate	0.0	no	1.1	slight	2.1	moderate	0.	no	5.7	serious
S7	2.	moderate	0.0	no	0.9	no	2.1	moderate	0.	no	5.9	serious
S8	4.	strongly	0.0	no	0.5	no	2.7	moderate	0.	no	4.3	strongl
S9	2.	moderate	0.0	no	0.5	no	3.6	strongly	0.	no	4.8	strongl

3.2.A.2. Metal Index (MI)

Another index is used to estimate the metal pollution of El-Manzala lake water for different utilizations. The metal index donates the trend evaluation of the present status by computing all the measured metals (Table 4). According to the metal index values, all the selected stations along the lake are seriously threatened with metal pollution for aquatic life usages (MI ≥ 1).

Table (4): Metal index of the measured metals in El-Manzala lake water for aquatic life utilizations

Stations	MI	Rank
1	16.29	Polluted
2	13.29	Polluted
3	10.45	Polluted
4	7.89	Polluted
5	12.09	Polluted
6	7.59	Polluted
7	11.99	Polluted
8	11.36	Polluted
9	7.90	Polluted

3.3. Sediment Heavy Metals

Most sediments in surface waters are derived from surface erosion and comprise a mineral component, which arises from the erosion of bedrock. They may also comprise an organic component, which arises during soil-forming processes (including biological and microbiological production and decomposition). An additional organic component may be added by biological activity within the water body [38]. Sediments are important sinks for various pollutants like trace metals. They can also act as a nonpoint source and have the potential to release the sediment-bound metals and other pollutants to overlying water, and in turn adversely affect aquatic organisms [39]. The contamination levels of the aquatic environment by heavy metals can be estimated by analyzing water, sediments and marine organisms [40].

The present study reveal that Fe content fluctuated between 23.6 and 25.9 mg/g. Iron varied in ranges 8.50-15.36 and 9.11-12.89 mg/g during summer and winter, respectively. Iron showed highly spatial significant differences. Iron concentrations fluctuated in wide ranges during the studied period. The trend of the distribution pattern was mainly attributed to the effect of domestic and agricultural wastes that discharged into the lake.The iron concentrations in drains were found in the ranges of 12.65-15.96 µg/g while the maximum value (15.96 µg/g) was recorded at Bahr El-Baqar drain in winter and the minimum value (12.65 µg/g) was recorded at Faraskour drain in winter.

The variations of manganese concentrations were varied in the ranges of 110.15-362.41 µg/g and 96.35-320.53 µg/g during summer and winter, respectively. The minimum value of Mn (96.35 µg/g) was recorded at station (9) during winter and the maximum one (362.41 µg/g) was recorded at station (5) during summer, which may be due to the agricultural, domestic sewage effluents and the effluents of the drain. Manganese values showed a highly spatial significant difference ($p< 0.01$). The manganese concentrations in drains were found in the ranges of 290.25-405.2 µg/g while the maximum value (405.2 µg/g) was recorded at Faraskour in winter and the minimum value (290.25 µg/g) was recorded at El-serw drain in summer.

The values of zinc varied in the ranges of 18.56-105.12 and 15.26-108.32 µg/g during summer and winter, respectively. There is a highly spatial significant difference for zinc ($p< 0.01$). The present results showed that, the lowest value of zinc (15.26 µg/g) recorded during winter at station (5) while the highest value (108.32µg/g) recorded during winter at station (3) may be due to domestic effluents from drains to the lake. The zinc concentrations in drains were found in the ranges of 72.65-176.25 µg/g while the maximum value (176.25 µg/g) was recorded at Bahr El-Baqar drain in summer and the minimum value (72.65 µg/g) was recorded at Faraskour drain in winter.

The variations of values of copper varied in the ranges of 5.58-18.98 and 8.56-15.98 µg/g during summer and winter, respectively. Copper values showed a highly spatial significant difference between stations ($p< 0.01$). The highest value (18.98 µg/g) recorded at station (3) during summer while the lowest value (5.58 µg/g) was recorded at station (8) during summer season. The copper concentrations in drains were found in the ranges of 13.45-25.12 µg/g while the maximum value (25.12 µg/g) was recorded at Bahr El-Baqar drain in summer and the minimum value (13.45 µg /g) was recorded at El serw drain in the same season. The highest value of lead (63.52 µg/g) recorded at station (1) during winter season may be attributed to the heavy agricultural run-off which contains fertilizers, agrochemicals and pesticides while the lowest value (5.65 µg/g) recorded at station (5) during summer season may be due to the uptake of Pb by phytoplankton and zooplankton, fish and other aquatic organisms in surface water but in drains varied between (9.12 - 65.24 µg/g). The values of Cadmium were varied in the lake sediment in the ranges of 1.09-4.02 and 1.29- 4.11 (µg/g) during summer and winter respectively. The maximum value 4.11 µg/g was recorded at station (1) in winter, while the minimum value 1.09 µg/g was recorded at station (4). The cadmium concentrations in drains were found in the ranges of 2.92-15.32 µg/g while the maximum value (15.32 µg/g) was recorded at Bahr El-Baqar drain in winter and the minimum value (2.92 µg/g) was recorded at Faraskour drain in winter as in table (5).

Table (5): Heavy metal concentrations in El Manzala lake sediment during 2015-2016

site	Fe mg/g		Mn µg/g		Zn µg/g		Cu µg/g		Pb µg/g		Cd µg/g	
	S	W	S	W	S	W	S	W	S	W	S	W
S1	9.16	12.3	278.	250.	105.	85.6	18.5	15.2	51.2	63.5	3.68	4.11
S2	8.56	12.8	302.	280.	96.5	85.2	16.8	15.2	38.1	49.1	2.89	3.12
S3	11.2	12.2	329.	295.	110.	108.	18.9	15.9	35.4	39.6	2.23	2.36
S4	10.0	11.1	308.	285.	29.5	25.3	9.16	12.5	7.62	9.59	1.09	1.29
S5	12.5	11.0	362.	320.	18.5	15.2	7.86	9.59	5.65	7.09	2.13	1.25
S6	11.2	10.1	320.	298.	54.3	45.3	14.2	12.3	12.1	13.2	1.50	2.02
S7	13.1	12.1	158.	140.	36.8	29.6	13.2	11.5	16.6	14.2	4.02	3.52
S8	8.96	9.11	305.	286.	22.1	18.2	5.58	8.56	11.1	16.8	1.12	1.62
S9	12.6	11.4	110.	96.3	65.5	75.4	17.4	11.5	16.2	21.0	3.18	4.08
Dr 1	15.3	15.9	354.	398.	176.	145.	25.1	18.6	58.5	58.3	13.5	15.3
Dr 2	13.2	14.2	315.	320.	165.	115.	18.4	15.8	12.1	9.12	6.25	8.25
Dr 3	12.7	14.0	389.	405.	125.	92.3	13.4	18.6	65.2	52.1	8.15	7.16
Dr 4	12.6	15.2	290.	325.	98.2	72.6	15.8	13.8	23.1	15.4	4.21	2.92

S: Summer; W: Winter

Table (6): Concentration of studied metals in El Manzal Lake sediment, geochemical background and the toxicological reference values for lake sediments (µg/g)

Metal	present result	Geochemical background		NOAA[1]				WCTMRL[2]	TRV[3]
		Shale standard[1]	Earth crust[2]	TEL	ERL	PEL	ERM		
Fe	8562-13190	46700	56300						
Mn	96.35-362.41	950	850						
Zn	15.26-110.25	95	70	124	150	271	410	50–250	110
Cu	5.58-18.98	40	55	18.7	34	108	270	20–90	16
Pb	5.65-63.52	20	12.5	30.24	46.7	112	218	10–100	31
Cd	1.09-4.11	0.3	0.15	0.68	1.2	4.21	9.6	0.1–1.5	0.6

Note: TEL= Threshold effect level; ERL; Effects range low, PEL; probable effect level, ERM; Effects range median, WCTMRL; and World common trace metal range in lake sediment, TRV; toxicity reference value

[1] NOAA (National Oceanic and Atmospheric Administration, 2009), Forstner and Whitman, 1981, Jones et al. 1997. **[41-43]**

Ecological Risk Assessment

Variety of methods have been developed for the risk assessment of heavy-metals in sediment, as sediments enrichment factor, index of geological accumulation and pollution load index. Various elements have different toxicological effects, among which some are highly toxic and others slightly toxic [44]. Ecological risk management provides policy makers and resource managers as well, as the public, with systematic methods that can inform decision making. A number of studies have applied this method [45-46].

Table (7): Terminologies for pollution classes on single and integrated indices

EF classes[1]		CF classes[2]		Igeo classes[3]			PLI[4]	
EF value	Pollution	CF value	Pollution	Igeo	Igeo class	Pollution	PLI	Pollution
EF < 2	depletion to mineral	CF < 1	low	< 0-0	0	Unpolluted	0	perfection
2 ≤ EF < 5	moderate	1 ≤ CF ≤ 3	moderated	> 0-1	1	Unpolluted to moderated	≤ 1	baseline levels
5 ≤ EF < 20	significant	3 < CF ≤ 6	considerable	> 1-2	2	Moderated polluted	> 1	polluted
20 ≤ EF< 40	very high	CF > 6	very high	> 2-3	3	Moderated to high polluted		
EF ≥ 40	extremely high			> 3-4	4	Highly polluted		
				> 4-5	5	Highly to extremely polluted		
				> 5-6	> 5	Extremely polluted		

(1)according to [47] (2) according to [48] (3)according to [49] and (4) according to [50].

Enrichment Factor (EF)

Enrichment factor (EF) is one widely used approach to characterize degree of anthropogenic pollution to establish enrichment ratios [51].

A component enrichment factor (EF) was initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater [52], but it was progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials [53]. To evaluate the magnitude of contamination in the environment, the enrichment factors (EF) were computed relative to the abundance of species in source material to that found in the earth's crust [54].

$$EF = (C_M/C_{X\text{sample}}) / (C_M/C_{X\text{Earth's crust}})$$

Where, C_M is the content of metal studied and C_X content of immobile element. Iron was chosen as immobile element because of natural sources. Many authors used iron to normalize heavy metals contaminants [55]. The reference Earth's crust of Fe, Mn, Zn, Cu, Cr, Pb and Cd were taken from Turekian and Wedepohl [56] as the background concentrations. The average abundance of Fe, Mn, Zn, Cu, Pb and Cd are 46700, 950, 95, 40, 20 and 0.3 µg/g, respectively.

Five contamination categories are generally recognized on the basis of the enrichment factor [47]. From another point of view, if EF value of an element is greater than unity; this indicates that the metal is more abundant in the sample relative to that found in the Earth's crust [57]. The EF values in the El-Manzala Lake sediment ranged between 0.95-1.15, 2.64-3.88, 1.18-2.75, 3.92-7.88 and 2.66-3.88 for Mn, Zn, Cu, Pb and Cd, respectively (Fig. 3) which signify the anthropogenic sources of Zn and Cu, in addition to the noticeable pollution with, Pb and Cd. This conclusion is in agreement with Zhang and Liu (2002) [58], who stated that EF values between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural processes. Whereas, EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic; and agreed with Atgin et al. (2000) [59] who declared that the sediment is considered contaminated at EF more than 5.

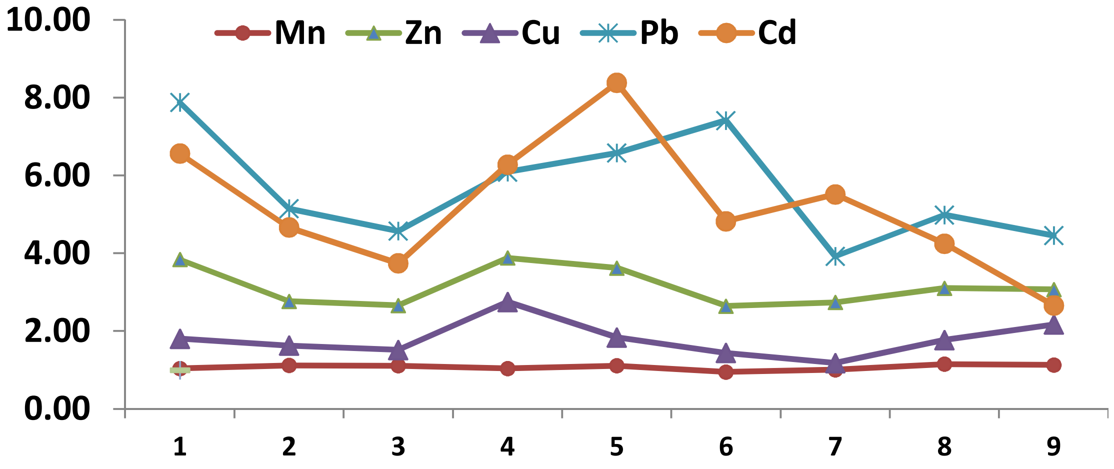

Fig (3) Enrichment Factor (EF) values of measured trace metals in Lake El-Manzala sediments

Index of geo-accumulation (I_{geo})

The geo-accumulation index I_{geo} values were calculated for the studied metals as introduced by Muller (1981) is as follows:

$I_{geo} = \log_2 (cn/1.5*bn)$

where **(cn)** is the measured concentration of examined element **(n)** in the sediment sample and **(bn)** is the geochemical background for the element **(n)** which is either directly measured in pre-civilization (pre-industrial) reference sediments of the area or taken from the literature (average shale value described by Turekian and Wedepohl (1961)[**56**]. The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations [**60**], as well as very small anthropogenic influences [**61**]. Muller proposed seven grades or classes of the geo-accumulation index [**62**]. Different geo-accumulation index classes along with the associated sediment quality are given in (Table 7); the I_{geo} class 0 indicates the absence of contamination while the I_{geo} class 6 represents the upper limit of the contamination. The highest class 6 (very strong contamination reflects) 100-fold enrichment of the metals relative to their background values [**63**]. On the other hand, Karbassi et al. [**65**] mentioned that

I_{geo} and EF failed to various degrees to designate the intensity of pollution.

I_{geo} values indicated that, the lake sediment (Fig. 4) is unpolluted with Fe, Mn, and Zn where, these trace metals exhibited a zero class. While Cu, Pb and Cd are classified as class (1) at the most stations, whereas I_{geo} values fluctuated from unpolluted to moderately polluted

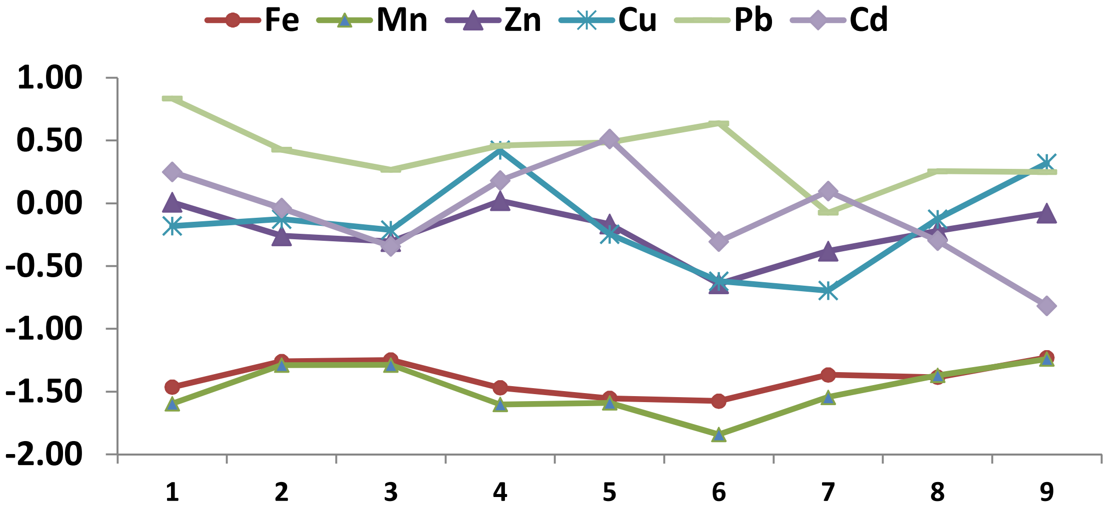

Fig (4): geo-accumulation index (I_{geo}) values of measured trace metals in El Manzala Lake sediment

Contamination Factor (CF)

The level of contamination of lake sediment or a sub-basin by given toxic substance (metals) suggested by Håkanson is often expressed in terms of a contamination factor calculated as follows [66].

Contamination Factor **(CF** = metal content in the sediment/background level of metal). The pollution grade of sediment according to CF values is given in Table 8. The CF values of all studied metals confirmed that the sediment of the lake is contaminated with Zn, Cu, Pb and Cd at the most station where 1 ≤ Cf ≥ 3 (moderated pollution). While, Fe and Mn were less than one (Low pollution)

Table 8: The Contamination factors of the studied trace metals in El Manzala Lake sediment.

Station	**Fe**	**Mn**	**Zn**	**Cu**	**Pb**	**Cd**
1	0.543	0.496	1.508	1.323	2.675	1.783
2	0.626	0.614	1.254	1.374	2.016	1.460
3	0.632	0.614	1.215	1.294	1.805	1.182
4	0.542	0.494	1.521	2.010	2.062	1.701
5	0.511	0.498	1.337	1.265	2.100	2.141
6	0.503	0.418	0.961	0.976	2.333	1.214
7	0.582	0.514	1.151	0.926	1.425	1.603
8	0.574	0.580	1.288	1.374	1.790	1.220
9	0.640	0.635	1.419	1.872	1.783	0.851

Pollution Load Index (PLI)

The pollution load index - PLI, proposed by Tomlinson *et al.* - has been used in the present study to measure PLI in sediments of Lake Nasser. The PLI for a single site is the *n*th root of the product of *n* contamination factors (CF values) [66].

PLI for a site = nth√CF_1* CF_2*…..CF_nt

Where, CF = contamination factor and n= number of metals

PLI for a zone = $n^{th}\sqrt{}$ $site_1 * site_2 *.....site_n$

Where, n equals the number of sites.

The pollution load index as presented in Fig. 5, delivers a simple, reasonable means for evaluating a site or area quality (0.0 indicates perfection, 1.0 indicate only baseline levels of pollutants present and > 1.0 would indicate progressive deterioration of the site) [**67**]. PLI values of sediments at the most sites of Lake are not polluted.

PLI can provide some understanding to the public of area about the quality of a component of their environment. It also indicates the trend spatially and temporally. In addition, it provides valuable information and advice to the policy and decision makers on the pollution level of the area [68].

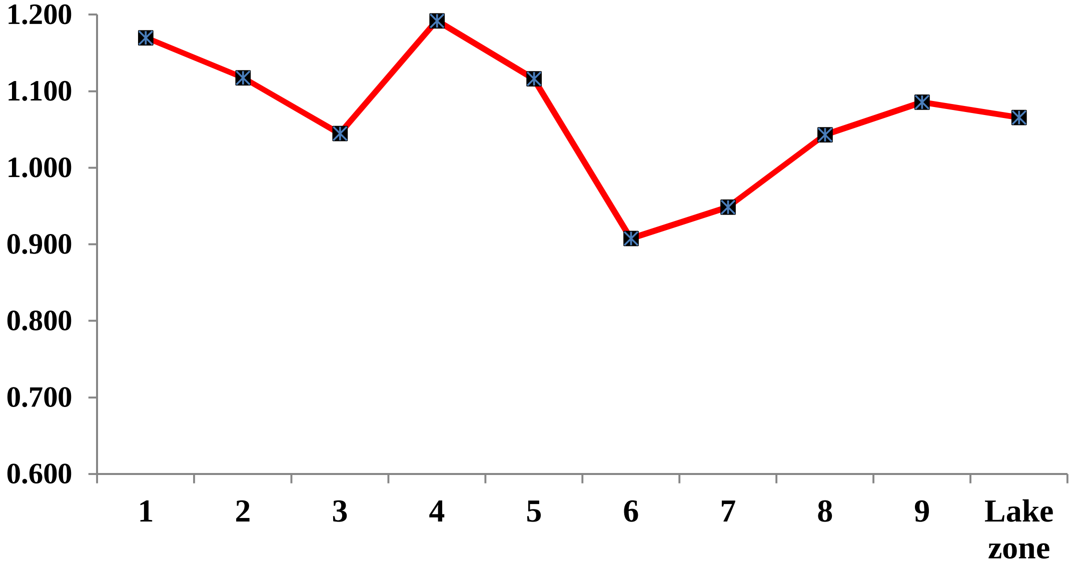

Fig (5): Pollution Load Index values of the analyzed metals in El-Manzala Lake sediment

PLI values of sediments in the different sites of Lake Nasser ranged from 0.908 to 1.192. The PLI of the zone or the whole investigated area of the lake however, was 1.066 which confirmed that the lake sediments are polluted.

4. Conclusion and recommendation

It could be concluded that the geospatial tools such as ordinary Kriging could be very helpful in evaluating and studying the spatial distribution of heavy metals in both water and sediment of El-Manzala Lake in Egypt. The obtained results clearly demonstrate that El-Manzala Lake water is highly contaminated with Fe, Cd, Cu, slightly contaminated with Zn and pb and not affected with Mn according to pollution index (PI). All investigated sites contaminated with heavy metals according to Metal Pollution index (MI). According to sediment, *enrichment factor (EF)* values in the El-Manzala Lake reveal the anthropogenic sources of Zn and Cu. In addition to the noticeable pollution with Pb and Cd. *Geo-accumulation index (Igeo)* Values indicated that the lake sediment is unpolluted with Fe, Mn, and Zn whereas, the trace metals exhibited a zero class. While Cu, Pb and Cd are classified as class (1) at most stations, whereas I_{geo} values fluctuated from unpolluted to moderately polluted. *Contamination factor* (CF) values confirmed that the sediment of the lake is contaminated with Zn, Cu, Pb and Cd at most station. *pollution load index (PLI)* of the whole investigated area of the lake was 1.066 which confirmed that the lake sediments are polluted. From these results we can conclude that the southern drains Bahr El-Baqar, Ramsis, El-Matria, Hadous, Faraskur and El-Serw play an important role in causing a severe pollution in El-Manzala Lake. Great efforts and cooperation between different authorities are needed to protect the lake from pollution and reduce the environmental risk. This can be achieved through the treatment of agricultural, industrial, and sewage discharge. Regular evaluation of pollutants in the lake is also very important.

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