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Distribution of Heavy Metals in Contaminated Water and Bottom Deposits of Manzala Lake, Egypt

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Abstract

The pollution of the El-Manzala lake bottom sediment is indicative of water and food-web guality in general. Twenty five samples were collected from both water and surficial bottom sediments. Collaborating analytical techniques have been employed to analyze group of environment-sensitive elements, including; Pb, Cd, Ni, Co, Cu, and Zn. The present study documents serious pollution by Cd, possibly as a result of using phosphate fertilizer. The average Cd content in the studied area is 17.5 ppm, which is about 36 fold the Maximum Permissible Limit (MPL=0.5 ppm) of soil. The highest concentration of Cd is 22.3 ppm, which is more than 45 fold the MPL. Cadmium is more mobile in aquatic environments than most other heavy metals. The areas around Port Said and El-Serw drain show marked pollution by most of the studied heavy metals. The main reason for such pollution is the industrial activities and agricultural drains. The unsupervised anthropogenic activities are the main causes of pollution in the studied lake. Routine program for monitoring the abundance and distribution of Cd, and Pb in the studied bottom lake sediments, water, biota and food chain should be imposed.

Keywords: El-Manzala lake; Bottom sediments; Pollution; Pb; Cd; Ni; Co; Cu; Zn; Egypt

Introduction

Manzala Lake is located in the northeastern edge of the Nile Delta. It is bound by the Mediterranean Sea to the north, Port Said to the northeast, the Suez Canal to the east, El-Dakahlia Governorate on the southwest, El-Sharkia Governorate on the south, and Damietta on the west (Figure 1). It is the largest brackish water body located in the northeastern shoreline of the Nile Delta, and it lies between latitudes; 31° 10" and 31° 40" N and longitudes; 31°50" and 32° 25" E. It is a shallow brackish water lagoon, with a depth ranging between 0.2 and 2 m.

At present, the lake area covers about ~1071 km², with maximum length of 64.5 km and maximum width of 49 km. The original area of El-Manzala lake was more than 1700 km² in 1900. The area of the lagoon has been reduced to 1200 km² by 1980 as a result of land reclamation. It water has a brackish nature, mixed with sea water through Boughaz El -Gamil opening (12.5 km west of Port Said) at the north eastern side of the lake.

Pollution sources

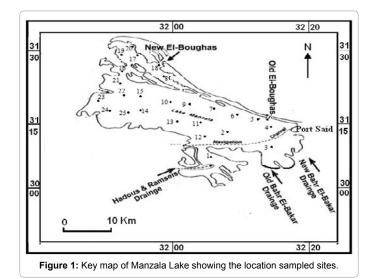
Manzala Lake is one of the most polluted lakes in Egypt. The sediments act as "sink" for metal contaminants, and risk increases with increasing metals leachability. The impact of such heavy metals abnormality may extend to involve the water quality and food web, and hence to the human health. In the studied area, source(s) 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.

The water quality and pollution of El-Manzala lake has been the objective of many authors El-Wakeel and Wahby [1], Abdel-Mouti [2], Abdel-Mout and Dowidar [3], El-Sabrouti [4], Hussein [5], Abdel-Satar [6], Dewidar and Khedr [7], Lotfy [8,9], Abdalla [10], Orabi [11].

The main objective of this study is mainly to assess the suitability of the lake for fish industry according the international constrains imposed by the Egyptian standards and the world-wide organizations such as; WHO, EPI, and FAO. Increasing awareness of pollution risk may support the implemented mitigation and remediation programs to face the rapid deterioration of this important marine ecosystem.

Materials and Methods

Samples of both water and surficial bottom sediments were collected from 25 locations represent the Manzala Lake during summer



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2014 (Figure 1). The sampled stations were chosen to cover the most of the studied area. Samples were essentially taken from the upper 50 cm of the Manzala Lake bottom sediments at water depth ranging from 20 cm to 2 meters. After air drying, samples were disintegrated and representative quotient was thoroughly pulverized to -100 mesh size, and then kept for chemical analyses. The chemical analyses were conducted on whole sediment samples for the trace elements; Pb, Ni, Co, Cu, Zn and Cd using atomic absorption spectrometry (Perkin-Elmer 3110, USA) with graphite atomizer HGA-600, after using the digestion technique according to the standard APHA [12]. The Physico-chemical parameters namely; pH, Ec, and total dissolved salts were measured. The former was measured by an Orient Research pHmeter, Model 20. Total dissolved salts, were determined also according to APHA [12]. The preparation of water and sediment for trace metal determination was carried out according the method described in FAO technical paper No.158.

Results and Discussion

Physico-chemical parameters

Water depth: Manzala Lake is characterized by its very shallow water due to silting up of sediment originated from the high load of discharged particles from the drains. The highest average depth was recorded at eastern portion of the lake (2 m), while the lowest depth (20 cm) was recorded at rest of the lake and in front of drain.

Hydrogen ion concentration (pH): The pH values play an important role as indicator of pollution levels and control many biological processes. The maximum value of pH (9.65) was recorded at the northern beach of the lake far away from the effects of discharges of the drains in southern side related to the high fertility and increase in the total count of phytoplankton (Figure 2A). The lowest pH value was recorded due the southwards of the lake (7.68) and attributed to the effect of pollution due to the liberation of CO₂ and H₂S during the decomposition of organic matters, in addition of load of discharges and organic matter.

Electrical conductivity (Ec): The electrical conductivity varies, in the lake water, between 3400 μ mhos/cm and 11900 μ mhos/cm, averaging 7680 μ mhos/cm. It increases gradually northwards, due to the inflow of sea water through the main connection between the lake and the sea and also to the inflow of agriculture wastewater at southwestern ward through El-Serw drain (Figure 2B).

Total dissolved salts (TDS): TDS in Manzala Lake was mainly affected by the drainage water discharged into the lake, the invasion of

sea water through the lake-sea connection, the high rates of evaporation, in addition to wind action. The highest value of total dissolved salts was recorded in the eastern portion of the lake near to El-Boughaz opening (17.56 mg/L) affected by sea water. This value decreases to its lowest value of 0.995 mg/L in the middle sector with an average of 4.47 mg/L (Figure 2C).

Heavy metals in lake water

The total heavy metals content of the investigated water are given in Table 1. The concentration of Cadmium ranges from 0 to 1.5 µg/L with an average of 0.4 µg/L. Lead ranges from 1.9 µg/L to 14.5 µg/L with an average 5.8 µg/L. Zinc ranges from 0.1 µg/L to 2.2 µg/L, with an average 0.9 µg/L while Nickel from 0.82 µg/L to 8.55 µg/L with an average 2.44 µg/L. Cupper ranges from 2.1 µg/L to 3.6 µg/L with an average 2.8 µg/L whereas Cobalt ranges from 1 µg/L to 2.17 µg/L with an average 1.45 µg/L (Figure 3).

Geochemical backgrounds

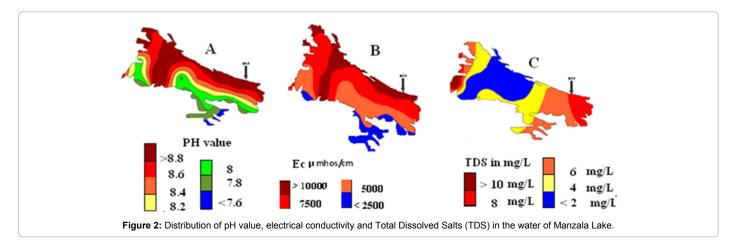
The comparison between the present data and the average earth's crust as quoted by McLennan and Taylor [13] is given in Table 2. The comparison suggests the following inferences:

- The average contents of Co, Pb, and Ni in the studied sediments (110, 79, 228 ppm) are about 6, 4 and 3 fold the average earth's crust, respectively
- Cd (from 5 to 22.3 ppm) is more than 20 and up to 65 fold the average earth's crust. Not like other heavy metal, Zn (130 ppm) is slightly higher than average earth's crust, while Cu (19.74 ppm in average) is eventually depleted to less than half the content of the crust.

Comparing with the US Public Health Service, which established the freshwater sediment quality guidelines in the form of level of probable effects, the studied sediments seem to be polluted at different levels (Table 3). The analyzed heavy metals (Co, Cu, Ni, Zn, and Cd, Pb) are not intimately correlated to each other as they have different speciation and sources. The elements; Pb. Ni, Co, Zn and Cd are strongly related to moderately correlate (Figure 4A).

The regional pollution index (RPI)

The degree of pollution of the El-Manzala lake bottom sediments can be calculated by normalizing the metals concentration to their Maximum Permissible Limits (MPL) used for the worldwide soil. In the given equation of the pollution index, the MPL of an element is



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1 8.5 2 7.1 3 7.1 4 10.4 5 14.5 6 8.2 7 8.9 8 5.5 9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	3.0 2.1 3.5 2.9	0.4 0.5 0.4 0.9	1.6 0.7 0.9 1.0	Nm 1.32 1.11	1.75 2.58
3 7.1 4 10.4 5 14.5 6 8.2 7 8.9 8 5.5 9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	2.1 3.5 2.9	0.4	0.9		
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6 8.2 7 8.9 8 5.5 9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7			1.0	1.44	5.25
7 8.9 8 5.5 9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	2.0	1.5	1.8	1.51	8.55
8 5.5 9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	۷.۷	0.7	0.9	1.37	4.12
9 4.8 10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	3.2	0.6	0.9	1.30	3.61
10 6.4 11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	3.0	0.3	0.5	1.68	2.06
11 4.6 12 4.0 13 2.9 14 3.9 15 5.7	2.7	0.0	0.2	1.52	0.93
12 4.0 13 2.9 14 3.9 15 5.7	2.9	0.2	0.3	1.00	1.65
13 2.9 14 3.9 15 5.7	3.1	0.0	0.6	1.64	0.93
14 3.9 15 5.7	2.7	0.1	0.2	1.28	1.34
15 5.7	2.8	0.2	0.2	1.28	0.82
	2.7	0.0	0.1	1.92	1.24
	3.0	0.1	0.5	2.17	2.16
16 6.0	3.0	0.1	1.4	Nm	1.85
17 4.0	2.8	0.1	0.9	Nm	0.82
18 5.7	2.9	0.1	1.1	Nm	1.75
19 5.7	2.9	0.2	1.2	Nm	2.16
20 10.0	3.6	0.8	2.2	Nm	5.8
21 1.9	2.4	0.3	0.9	1.54	Nm
22 2.1	3.6	0.8	1.4	1.62	Nm
23 2.0	2.5	0.4	0.5	1.15	Nm
24 2.7	2.4	0.4	1.1	1.29	Nm
25 2.8	2.7	0.3	0.9	Nm	Nm
Average 5.8	2.1				
Maximum 14.5		0.4	0.9	1.45	2.44

Nm: Not measured

Table 1: Concentrations of trace elements in surface water of Manzala Lake (µg/L).

considered as the "pollution standard level or goal". The index of an individual pollutant is calculated as follows:

Index = $\frac{\text{Pollution concentration} \times 50}{\text{Pollutant standard level or goal}}$

For each region, the highest calculated index is used as the RPI for that region. An RPI of 50 corresponds to the relevant standard/goal. The RPI is categorized as low, medium or high, as follows:

- Low pollution index from 0 to 24
- Medium pollution index from 25 to 49
- High pollution index 50 or higher.

Table 3 summarizes the RPI of the studied Manzala Lake bottom sediments. It can be concluded that the studied area is exposed to high pollution levels by Cd, Pb, Ni and Co, whereas Zn and Cu display low degree of pollution.

Heavy metals in lake sediments

The following is a brief discussion on the environmental status of organic matter and some metals that may bear some risk or endanger on human environment beside the geochemical distribution maps of potentially toxic metals. The total heavy metals content of the investigated sediments are given in Table 4.

Organic matter: The organic matter content ranges between 1.24 and 12.14%, with an average of 6.45%. The lowest value was recorded in the eastern portion of the lake, but the content increases toward the western side where el-Serw agricultural drain is located (Figure 5A).

Lead (Pb): Among all metals; Pb, Cd and Zn are in the closest relationship to humans; however, Pb is damaging to the human body. In the present work, the total lead content ranges from 19.6 to 153.6 ppm, with an average of 78.48 ppm (Figure 4B). The lowest value is recorded at middle portion of the lake while the highest values are recorded near el-Serw agricultural drain and, also, at eastern portion of the lake where the industrial region in Port Said country (Figure 5B).

The MPL of Pb in the worldwide soils is 20 ppm. According to the Agency for Toxic Substances and Disease Registry, soil contamination by lead from mine tailings may be less effective in increasing PbB (blood lead) levels than its lead contamination derived from urban lead pollution.

Cadmium (Cd): It is more mobile in aquatic environments than most other heavy metals, e.g., Pb. Igneous and metamorphic rocks have low values of Cd from 0.02 to 0.2 ppm, whereas sedimentary rocks may have higher values (0.1 to 25 ppm). According to Kabata-Pendias



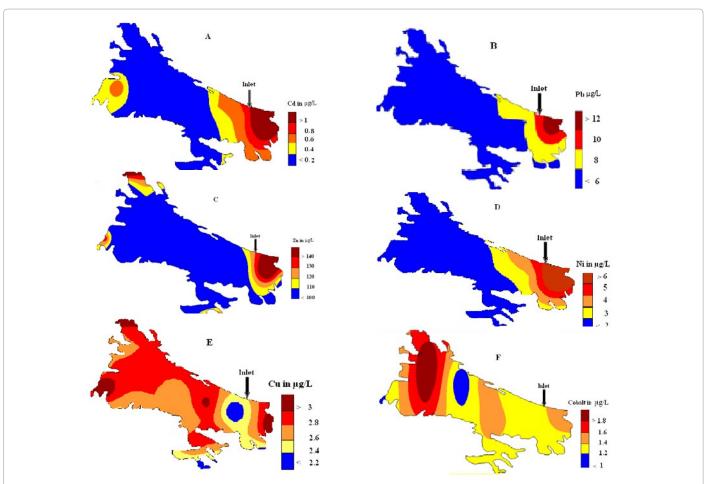


Figure 3: Spatial distribution map of the analyzed potentially toxic metals in the studied lake water (A) Cadmium, (B) Lead, (C) Zinc, (D) Nickel, (E) Cupper and (F) Cobalt (µg/L).

Elements	Present Study	Abdalla (2003)	Ghallb (2007)	Lotfy (2007)	Average share of Mason and Moor, 1982	Solomns & Forest (1984)	Fresh water sediments (USPH, 1997)	Earth crust McLennan and Taylor (1999)
Pb	78	9	21	51	20	19	20	20
Cu	20	40.5	19.33	20.7	50	33	45	25
Cd	18	Nd	28	21	0.3	0.11	1	0.5
Zn	130	71.5	44	62	90	95	<100	70
Ni	228	46.3	Nd	49	80	Nd	45	20
Со	110	19.5	Nd	Nd	20	Nd	Nd	10
Fe	10799	34500	3220	58000	47000	4100	Nd	Nd

Table 2: Average heavy metals of the present work compared with average earth crust McLennan and Taylor [13], and averages of published data (contents are given in ppm).

[14], the Maximum Permissible Limit (MPL) of Cd in cultivated soil is 0.5 ppm. The Department of Health and Human Services (DHHS) has determined cadmium and cadmium compounds as carcinogens; therefore, the Environmental Protection Agency (EPA) has set a limit of 5 ppb of cadmium for drinking water. In the present study, the Cd content ranges from 5.9 to 22.3 ppm with an average value of 17.5 ppm. The frequency distribution of Cd is unimodal with maximum at about 15-20 ppm (Figure 4C). The distribution pattern is strongly skewed towards the higher concentrations. Therefore, the average content of Cd in the study area is more than 36 fold the MPL of soil as quoted by Kabata-Pendias. While the highest Cd content (22.3 ppm) is more than 48 fold.

Generally, Cd being more mobile in aquatic environments than most other heavy metals, it can be a serious pollutant for the lake bottom sediments. It is mostly related to phosphate fertilizers at El-Serw agriculture drain, also possible source where Cd is the combustion of fossil fuel and some industrial activities at western portion of the studied lake (Figure 5C).

Cobalt: Co content ranges between 71 and 164 ppm, averaging 110 ppm (Figure 4D). This average value is more than two fold of the MPL

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Elements	Present study (ppm)	MPL (ppm)	RPI	Type of pollution
Cd	18	0.5	1754	High
Cu	20	100	10	Low
Ni	228	100	114	High
Со	110	50	110	High
Zn	130	300	22	Low
Pb	78	20	196	High

Table 3: Average heavy metals of the present work compared to the average of the Maximum Permissible Limit (MPL) in the worldwide soils [14] and Regional Pollution Index (RPI).

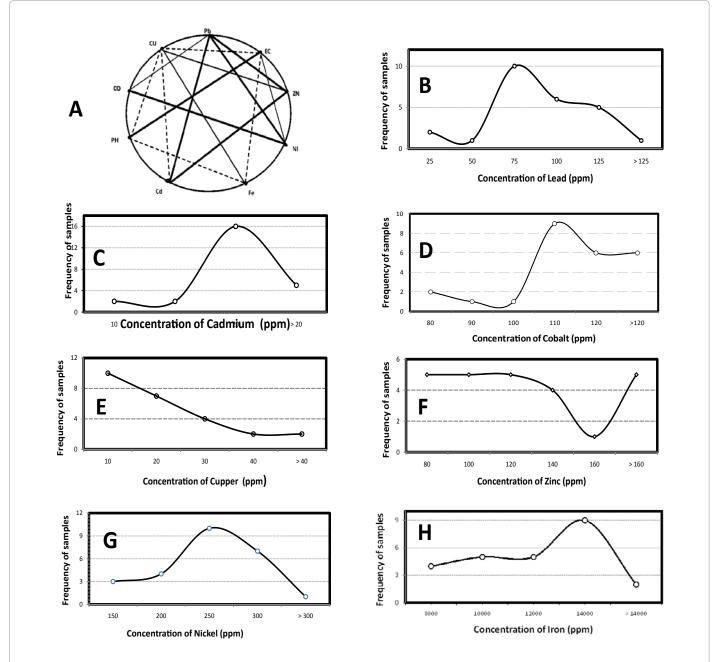


Figure 4: Correlations among the analyzed heavy metals (A). The intensity of lines corresponds to the strength of the correlation coefficient. The dotted line means weak or reversed relation. Frequency distribution, in ppm, of lead (B), cadmium (C), cobalt (D), copper (E), zinc (F), nickel (G) and iron (H) in the studied area.

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Station No.	Pb	Cu	Cd	Zn	Ni	Co	Fe	om
1	79.8	6.9	18.5	76.3	198.8	104.5	6219	7.6
2	22.2	2.9	14.3	70.3	149.8	81.3	6346	8.1
3	83.7	5.5	19.5	97.4	258.1	119.1	6518	5.5
4	56.6	5	16.2	65.1	187.7	101.3	7058	4.9
5	124.3	10.4	22.1	120.6	264.7	125.1	8028	1.6
6	67.4	12.4	18.4	164.1	218.8	107.1	9252	3.7
7	124.3	13.7	20.6	111.3	268.5	126.4	9290	6.9
8	52.1	5.3	16.6	87.3	210.9	105.6	9322	8.3
9	71	3.3	19	67.4	186.4	92.7	9650	4.0
10	82.1	4.7	19.9	73.5	216.4	106.5	10520	8.8
11	90.2	8.5	19.8	94.9	248.6	112.8	10730	4.6
12	91	8.5	19.2	109.5	248.6	114.6	10780	4.6
13	63	10	17.6	114.8	232.3	108.9	11060	4.1
14	107.4	26.5	21.3	106.4	255	115.7	11380	11.6
15	67.9	15.4	17.3	95.5	237.5	109.1	12150	7.5
16	62.8	20.8	18.5	127.7	241.9	111.3	12210	12.1
17	63.2	78.4	5.9	218.2	117.7	70.8	12300	1.2
18	67.5	10.1	17.9	95.8	249.7	115.5	12650	7.3
19	108.5	24	22.3	209.3	294.3	131.7	12850	9.4
20	32.8	16.8	16.5	104.4	196.9	102.8	12910	6.0
21	19.6	37	5.9	124.6	137.3	70.8	13140	3.6
22	67.9	29.8	17	163.9	260.8	120.2	13510	7.2
23	118.8	17.8	22	139.7	301.5	164.4	13890	9.7
24	153.6	86.5	14.8	461.8	231.4	107.5	14080	10.6
25	84.3	33.2	17.4	150.2	281.3	131.4	14130	2.6
Average	78.5	19.7	17.5	130.0	227.8	110.3	10798.9	6.5

Table 4: Concentrations of trace elements in bottom sediments of Manzala Lake.

recorded for the worldwide soil (50 ppm) as quoted by Kabata-Pendias [14]. The content of Co increses tword the eastern side of the studied lake, due to industerial activites in Port Said country. Other focuse of polution has been distinguihed near El-Serw agricultural drain (Figure 5D) [15].

Copper: Its content ranges from 2.9 to 86.5 ppm, averaging 19.7 (Figure 4E). The highest content is almost equal to the MPL (100 ppm). According to Kabata-Pendias [14], the simple frequency distribution of Cu in the studied sediments indicates that 80% of the analyzed samples contain below 30 ppm, while 20% of the samples contain >30 ppm (Figure 5E). It was noticed that Cu content increases gradually toward the south eastern portion of the lake due to Bahr el Baqar drain, with several anomalous patches near the main cities and close to Damietta country, which seems to be the main industrially polluted [16,17].

Zinc: In the studied lake ranges between 65.1 and 461.8 ppm, averaging 130 ppm. The content increases due south eastern portion, due to industerial activity in Port Said country (Figure 5F).

Nickel: It is considered as a very toxic element. In the present study, Ni content ranges between 117 and 302 ppm, averaging 228 ppm. This average value is more than two fold the MPL recorded for the worldwide soil (100 ppm), as quoted by Kabata-Pendias [14]. The frequency distribution of the Ni is unimodal with maximum at about 200-250 ppm. Ni is concentrated at the eastern part of the lake due to industrial activity near Port Said. Fe also accumulates at the northwestern side of the studied area, close to El Serw drain and the industrial region of Damietta (Figure 5G) [18].

Iron: In the present study, Fe content ranges between 6219 ppm and 14130 ppm, averaging 10800 ppm. The frequency distribution of the Fe is unimodal with maximum at about 12000-14000 ppm. Fe content is concentrated at southeastern portion of the lake towards

Bahr el Baqar drain, also Fe accumulated at northwestern side where Mohib drain and Damietta industrial region (Figure 4H) [19].

Total heavy metals

In general, the heavy metals; lead, copper, cadmium, zinc, cobalt and nickel, produce their toxicity by forming complexes or "ligands" with organic compounds. In the studied sediments the heavy metals distribution pattern is not uniform and it seems to be more likely related to anthropogenic activities. It shows gradual increase of pollution towards el-Serw agricultural drain and the second order level of pollution is recorded near the main cities where Industrial district in Port Said country at eastern portion of the lake and Damietta country at the west of the lake (Figure 6) [20-22].

Conclusions

In northern lakes of Egypt Manzala lake receives greet quantity of agricultureal, industerial, municipal annd domestic wastwater, in addition to navigation and fishing activities. Generally, the highest concentrations of Cd, Pb, Ni and Zn in water were observed in the eastern portion of the lake where industrial zone of Port Said country whiles the lowest values were recorded at the western portion of the lake. Highest Cu and Co values were recorded in the western area towards el-Serw agricultural drain. The relative order of abundance of the potentially toxic metals in the lake's water is; Pb>Cu>Zn>Cd. The present work is based on chemical analysis data on the bottom sediments of the Manzala Lake, relative to average earth's crust, the lake sediments are markedly enriched in Cd, Ni, Co, and Pb, and slightly enriched in Cu and Zn. The calculated pollution index nominates Cd, Ni, Co and Pb as pollutants of high level, while Cu and Zn are at low level. Generally, the distribution of heavy metals in Manzala Lake revealed that the agricultural drains represented by El-Serw drain and the Industrial district represented by Port Said country and

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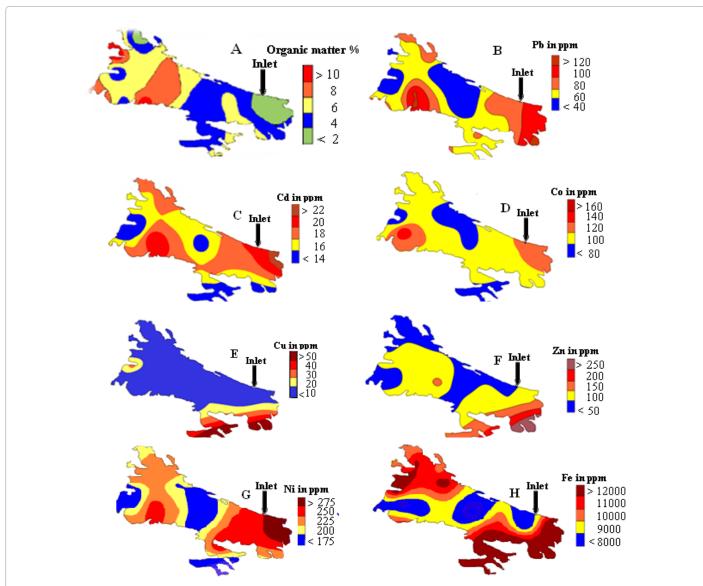
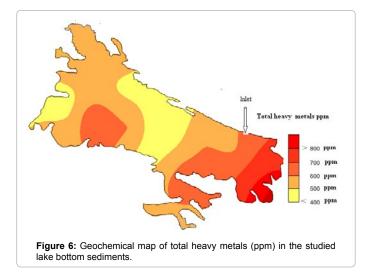


Figure 5: Geochemical maps of heavy metals in the studied bottom lake sediment: (A) Organic matter %, (B) Lead, (C) Cadmium, (D) Cobalt, (E) Cupper, (F) Zinc, (G) Nickel, and (H) Iron (ppm).



fishing boats seem to be main source of pollution. The relative order of abundance of elements in lake water is Pb>Cu>Zn>Cd, while the relative order in bottom lake sediments is Fe>Ni>Zn>Co>Pb>Cu>Cd.

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