



Distribution of essential heavy metals in the aquatic ecosystem of Lake Manzala, Egypt



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ABSTRACT

Lake Manzala is the largest and most productive lake of Egypt's northern coastal lakes and has socio-economic impacts. Pollution by heavy metals is the most significant type of pollution worldwide, particularly in Lake Manzala, which receives mixed discharges from densely populated areas. Water samples were collected at twelve sites around the lake in winter and summer of 2015. Samples of *Eichhornia crassipes* were collected in the winter, and *Oreochromis niloticus* samples were collected at two sites (8 and 10). V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were analysed in these samples using inductively coupled plasma-mass spectrometry. The average metal concentrations were below the internationally accepted upper permissible limits and are improved compared to those in previous studies. However, the metal concentrations at the eastern and southeastern sites were higher than the allowable limits due to multiple waste discharges. Pollution assessment using pollution risk indicators indicated low to moderate concentrations of metal enrichment in the sediment and biota of the lake, except at sites near the eastern and southeastern drains; these latter sites were considered to be hazardous and should be taken into account in the current development efforts of the lake. Complete removal of floating plants transported by drains is recommended.

1. Introduction

Water pollution has become a global problem, especially pollution by heavy metals because they do not decay into harmless end products and are toxic to many forms of life [1]. Heavy metals accumulate in food chains, posing a major threat to the environment and public health [2].

Some heavy metals, such as V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, are essential to biota at trace levels and are recommended as daily dietary supplements [3]. However, their levels in aquatic ecosystems should not exceed the upper permissible limits (UPLs); otherwise, they are considered contaminated. UPLs vary depending on the water type and use, the country (Supplementary Materials, Table S1), and the harmful synergistic effects of the contaminant on living organisms [4]. Elevated levels of heavy metals in water and sediment may lead to their uptake by biota. For example, plants growing in a polluted environment accumulate toxic metals at high concentrations, which ultimately pose a serious risk to human health when consumed. Plants absorb these metals from the

ground and water in polluted environments. According to the heavy metal concentrations, five categories of water were proposed, from category I, which is pure fresh water suitable for all species of fish, to category V, which can be used for only mineralization applications [5].

Sparingly water-soluble heavy metal ions are easily adsorbed and accumulated in sediments even at trace levels [6]. Thus, coastal sediments are considered the eventual sink for trace metals. However, some heavy metals are mobilized back into the water depending on the physicochemical conditions such as the salinity, pH, redox status, and organic matter decay rate [7]. These conditions are quite variable in coastal Lake Manzala, located in the northeastern part of the Nile Delta between the Damietta Branch of the Nile River and the Suez Canal (Fig. 1), especially during the ongoing development in the area including depth increases and sediment removal.

The Mediterranean Sea is connected to the northern end of the lake through narrow channels. Although the lake is considered the largest lake of the Nile Delta lakes, its area is decreasing gradually and

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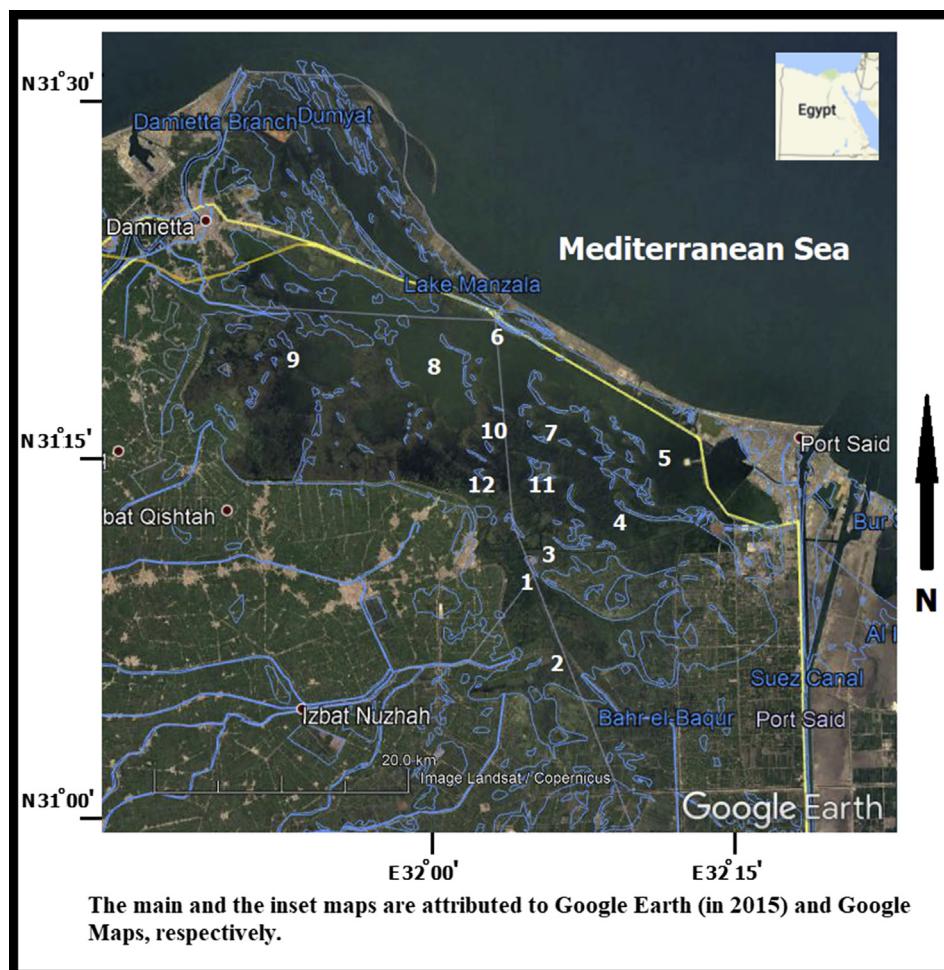


Fig. 1. Map of sampling sites of Lake Manzala, Egypt during 2015.

continuously. Over the last century, large-scale land reclamation has reduced the 750,000-feddan lake area in 1900, to less than 14%. Additionally, approximately 67% of the lake is less than 100 cm deep [8]. The lake was composed of intermittent basins and included approximately one thousand small islands, during the time of this study. Heavy metals accumulate in the sediments and biota of Lake Manzala, which can be considered sensitive indicators for monitoring the pollution status. The most common anthropogenic metal sources are industrial waste, oil contaminants and sewage water flowing through different drains that empty into the lake [9]. These drains are located in the eastern and southeastern regions of the lake. Their water streams are fed by discharges from various sources, such as agricultural discharges, to the Ramsis and Hadus drains in the southeastern region and the Inania, Faraskour and El-Serw drains in the southwestern region and domestic discharges to the Alhuria drain in the eastern region. However, the Bahr Elbaqur drain, located in the eastern region, is fed by many different waste discharges [10, 11].

The regular evaluation of heavy metal concentrations in ecosystems is important for assessing the pollution status, especially when using geo- and bioaccumulation indices. There are mathematical models for translating water quality data into simple evaluation terms (e.g., excellent, good, bad, etc.), with which the water quality classes are better defined [12, 13, 14, 15, 16]. For example, the enrichment factor (EF) describes the sediment enrichment of an element compared with its natural abundance in the earth's crust [12], whereas the geoaccumulation index (I_{geo}) indicates the relative contamination of sediment by an element in a given region compared with the element concentration in a pristine location [13]. The potential ecological risk index (RI), another important

pollution index, considers both the geoaccumulation ratio and the potential toxicity of the element [14]. Additionally, the bioaccumulation factor (BAF) reveals the interactions between metals in water and plants and the relative rates of plant intake and elimination [16].

Although, several recent studies have reported levels of heavy metals in Lake Manzala compared with the UPLs [17, 18, 19], none have evaluated the pollution risk in terms of pollution indices. The local authorities are currently launching an ambitious project to develop and rehabilitate the lake to meet standards for a clean environment by 2020 and it is necessary to describe the pollution status prior to this project as a baseline for comparison. In a previous work, the physicochemical properties of Lake Manzala in 2015 were reported [10]. The current research aims to assess the pollution impact from essential heavy metals, during the same period on the aquatic ecosystem of the lake and apply accumulation and risk assessment indices to the data.

2. Materials and methods

2.1. Description of the study area

Lake Manzala is a brackish coastal lake connected to the Mediterranean Sea via the following five outlets, allowing for the exchange of water and biota between the two water bodies: El-Soufara, El-Boughdady (Damietta), El-Gamil, new El-Gamil, and El-Etisaal Channel (Port Said) [17]. Sites (shown in Fig. (1)) were selected to give an indication of the distribution of heavy metals around the lake. Water, sediment and water hyacinth (WH; *Eichhornia crassipes*) samples were collected at 12 Sites that had been previously characterized: 1 (El-Matteriah), 2 (Genka), 3

(Ras Set Elbanat), 4 (Elbashtir), 5 (El-Gamil), 6 (Temsah), 7 (Kassab), 8 (Alhomra), 9 (Elzarka), 10 (Bahr Kromlos), 11 (Legan), and 12 (Deshdy) [10]. *Tilapia (Oreochromis niloticus)* samples were collected at two sites (8 and 10).

Sites (1)–(3) are influenced by agricultural discharge from the Ramsis and Hadus drains. Site (4) is influenced by various discharges from the Bahr Elbaqur drain. Site (5) is affected by seawater and sewage from the El-Qabuty and El-Gamil outlets and Alhuria drain, respectively. Site (6) is affected by seawater from the El-Dibah outlet. Site (9) is affected by agricultural discharges from the Inania, Faraskour and El-Serw drains. Site (12) is affected by agricultural discharge from the El-Gamaliyah and El-Matariya drains. Sites (7), (8) and (11) are not influenced by direct discharges [10].

2.2. Sample collection

Water samples were collected on 10 February, 2015 (winter) and 15 September, 2015 (summer) using an automatic water sampler, filtered through ashless filter paper, and then stored frozen in polyethylene bottles at -15°C . WH, sediment and fish (10–15 cm length) samples were collected on 10 February 2015, washed in the field and transported chilled to the laboratory in polyethylene bags where they were stored at -15°C .

2.3. Analytical methods

Standard solutions of the metal ions V, Cr, Mn, Fe, Co, Ni, Cu, and Zn at 1 mg mL^{-1} from Perkin Elmer were used for calibration after appropriate dilutions with high-purity water (HPW). HPW was also used for diluting samples and blanks.

The frozen samples were thawed prior to analysis. The samples homogeneity were well considered. Water samples (1 L) were concentrated at pH 3.5–4.0 by applying the APDC/MIBK extraction procedure [20]. The solvent was evaporated from the collected extracts, and the residues were digested in 65% nitric acid and then dried until near dryness. The final volume was adjusted to 10 mL with deionized water. The sediment samples were dried at 60°C in air for one month and then subjected to microwave-assisted nitric acid digestion (SW846 3051) [21]. Plant samples (leaves) were digested in nitric acid with microwave irradiation according to the method of Xing and Yeneman [22]. Fish muscles or gills were minced, well mixed, weighed (wet weight of 1–2 g), and digested in nitric acid [23].

2.4. Quality control

Laboratory quality control (QC) of the metal analyses was conducted as previously reported [24] with certified reference materials from NIST: SRM 2709a, San Joaquin Soil; SRM 2710a, Montana Soil I; and SRM 2711a, Montana Soil II [24].

2.5. Apparatus

Inductively coupled plasma-mass spectrometry (ICP/MS) was performed on a NexION 300D system (Perkin Elmer, New York, USA). The instrumental conditions are shown in Table (S2). Deionized water was obtained from a water purification system type Purelab Option Q15 from ELGA LabWater (England). A microwave digestion system (Ethos One, Milestone, Sorisole, Italy) was used to digest the samples of sediments, plants and fish.

2.6. Pollution assessment

2.6.1. Enrichment factor

The EF was calculated according to Eq. (1) [12]:

$$EF = \frac{(X_s^i/X_s^{Fe})}{(X_{EC}^i/X_{EC}^{Fe})} \quad (1)$$

X_s^i is the concentration ($\mu\text{g g}^{-1}$) of a heavy metal in the sediment sample, X_s^{Fe} is the concentration ($\mu\text{g g}^{-1}$) of iron as an immobile metal in the sample and (X_{EC}^i/X_{EC}^{Fe}) is the natural abundance ratio of the metal ion (i) in the earth's crust to the immobile reference metal Fe [25]. The average natural abundances of V, Cr, Mn, Fe, Co, Ni, Cu, and Zn are 97, 1000, 92, 54000, 17.3, 47, 28 and 67 ng g^{-1} , respectively.

2.6.2. Geoaccumulation index

The contamination level of sediments was assessed by the geoaccumulation index (I_{geo}) according to the formula developed by Müller and Süss [13]:

$$I_{geo} = \log_2 \frac{X_s^i}{1.5 X_r^i} \quad (2)$$

X_r^i is the background level of a given element (i) in a selected reference background, which was the Egyptian coast of Mediterranean Sea in the present study [26, 27].

2.6.3. Ecological risk evaluation

The RI was evaluated to assess the degree of ecological risk posed by heavy metals in the samples and was determined according to Hakanson [14]. The RI was calculated by the following formulas:

$$X_r^i = \frac{X_s^i}{X_r^i} \quad (3)$$

$$E_r^i = T_r^i \cdot X_r^i \quad (4)$$

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

X_r^i is the contamination factor for a given heavy metal (i) and X_s^i is the preindustrial concentration of that heavy metal in the sediment ($\mu\text{g g}^{-1}$) obtained from reported data for the Egyptian coast of the Mediterranean Sea [26, 27] and the Nile River in Damietta [28, 29]. The RI is the sum of the potential risks of individual heavy metals, E_r^i is the potential risk of an individual heavy metal. T_r^i is the toxic response factor of each element: V = 2, Cr = 2, Mn = Fe = 1, Co = Ni = Cu = 5 and Zn = 1 [14].

The pollution load index (PLI) of each site was evaluated as indicated by Tomilson et al. [15].

$$PLI = (X_r^1 \cdot X_r^2 \cdot \dots \cdot X_r^n)^{1/n} \quad (6)$$

where, n is the number of metals.

2.6.4. Bioaccumulation factor

The bioaccumulation factor (BAF) of each metal in plants was calculated by dividing the total content in the plant (X_p^i) by the total content in water (X_w^i) [16]:

$$BAF = \frac{X_p^i}{X_w^i} \quad (7)$$

2.7. Statistical analysis

A bivariate two-tailed Pearson correlation test was used to evaluate the significant difference in the concentrations of metals at different study sites and previously reported water quality parameters [10]. A probability of a level of 0.05 or less was considered significant [30].

3. Results

3.1. Essential heavy metal analysis

3.1.1. Water

Table 1 shows the heavy metal ions V, Cr, Mn, Fe, Co, Ni, Cu and Zn concentrations in the water of Lake Manzala in 2015. In winter, the concentrations were 6.45–70.02, 6.25–145.88, 2.68–31.84, 356.7–3148.4, 1.19–8.11, 13.99–51.54, 16.25–95.71, and 114.65–853.3 $\mu\text{g L}^{-1}$, respectively. The highest concentrations of Cr, Fe, Co, and Cu were observed in winter at site (12), those of V and Zn were observed at site (3), and those of Mn and Ni were recorded at sites (1) and (4), respectively. The lowest values of Cr, Fe, Cu and Zn were recorded at site (8), whereas those of V, Mn, Co and Ni were recorded at sites (7), (2), (3) and (6), respectively. The metal concentrations decreased in the following order: Fe > Zn > Cu > Ni > V > Cr > Mn > Co. The site heavy metal contamination decreased in the following order (12) > (4) > (1) > (3) > (9) > (5) > (10) > (2) > (7) > (11) > (6) > (8).

In summer, the concentrations of V, Cr, Mn, Fe, Co, Ni, Cu and Zn in the water of Lake Manzala were 21.33–94.79, 3.54–10.04, 1.69–7.96, 135.9–874.1, 0.54–1.39, 17.38–45.22, 21.25–133.8 and 43.33–168.4 $\mu\text{g L}^{-1}$, respectively. The highest values of Cr, Mn, Fe, Co, Ni and Zn were recorded at site (1), whereas the highest values of V and Cu were recorded at site (12). The lowest values of Mn, Fe and Co were recorded at site (6), whereas those of V, Cr, Ni, Cu and Zn were recorded at sites (2) (10) (11), (5) and (3), respectively. In summer, the site heavy metal contamination decreased in the following order: (1) > (2) > (3) > (12) > (4) > (5) > (10) > (9) > (11) > (7) > (6) > (8). The metal ion concentrations decreased in a similar to that in winter. The total heavy metal load in winter (17.782 mg L^{-1}) was almost three times higher than that in summer (6.268 mg L^{-1}). Figure (2) shows the relative abundances (%) of the metal ions in the water at different sites with respect to the highest values of each metal.

3.1.2. Sediments

Sediment samples were analysed for the target heavy metal ions, and the results are presented in Table 2. The observed concentration ranges of

V, Cr, Mn, Fe, Co, Ni, Cu and Zn were 13.62–107.9, 7.98–227.5, 233.0–1152, 560.2–28043, 3.55–23.28, 10.01–62.73, 8.49–128.63 and 9.21–310.0 $\mu\text{g g}^{-1}$, respectively. The highest values of V, Cr, Fe, Ni, Cu and Zn were recorded in the sediments at site (4), whereas the highest values of Mn and Co were detected at sites (10) and (1), respectively. The lowest values of Cr and Zn were detected in the sediments at site (11), whereas those of V, Mn, Fe, Co Ni and Cu were recorded at site (3). The sediment metal loadings decreased in the following order: (4) > (1) > (2) > (12) > (10) > (8) > (5) > (7) > (6) > (9) > (11) > (3). The metal concentrations in sediments decreased in the following order: Fe > Mn > Zn > V > Cr > Cu > Ni > Co. Figure (3) shows the relative abundances (%) of the metal ions in the sediments at different sites with respect to the highest abundances of each metal.

3.1.3. Water hyacinth

Table 3 shows the concentrations of V, Cr, Mn, Fe, Co, Ni, Cu and Zn in WH samples from Lake Manzala collected in winter 2015. The highest values of V, Cr, Fe and Co were recorded at site (4), the highest values of Cu and Ni were detected at site (10), and those of Mn and Zn were observed at sites (11) and (1), respectively. The lowest values of Cr, Fe, Ni and Zn were recorded at site (8), whereas those of V, Mn, Co and Cu were recorded at site (12). The order of site heavy metal contamination decreased in the following order (11) > (4) > (2) > (6) > (7) > (10) > (1) > (3) > (9) > (5) > (8) > (12). The heavy metal concentrations in WH decreased in the following order: Mn > Fe > Zn > Cu > Cr > V > Ni > Co. Figure (4) shows the relative abundances (%) of the metal ions in WH at different sites with respect to the highest abundance of each metal.

3.1.4. Fish

Table 4 shows the metal contents in the gills and muscles of *O. niloticus* caught at sites (8) and (10). The metal concentrations decreased in the following order: Fe > Mn > V > Zn > Cu > Ni > Cr > Co. The average metal concentrations in the gills and muscles were 24.134 and 2.338 $\mu\text{g g}^{-1}$, respectively, whereas the total investigated metal contents at sites (8) and (10) were 13.738 and 12.735 $\mu\text{g g}^{-1}$, respectively.

Table 1
Concentrations ($\mu\text{g L}^{-1}$) of heavy metals in water of Lake Manzala.

Site	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
In winter								
1	46.12 ± 1.52	16.5 ± 0.42	31.84 ± 0.48	1122.8 ± 16.8	5.36 ± 0.08	41.6 ± 0.70	81.44 ± 0.90	544.4 ± 2.2
2	57.7 ± 0.52	26.46 ± 0.66	2.68 ± 0.04	386.3 ± 9.6	1.22 ± 0.02	44.78 ± 1.12	52.30 ± 0.88	689.2 ± 6.2
3	70.02 ± 0.56	10.42 ± 0.04	4.78 ± 0.04	824.16 ± 14.8	1.19 ± 0.02	40.52 ± 0.44	83.22 ± 0.050	853.3 ± 6.0
4	33.94 ± 1.06	20.64 ± 0.28	8.66 ± 0.10	1458.3 ± 20.2	4.80 ± 0.06	51.54 ± 0.46	78.86 ± 0.94	440.1 ± 6.6
5	18.08 ± 0.26	6.98 ± 0.22	7.38 ± 0.08	1042.2 ± 14.6	1.88 ± 0.06	18.46 ± 0.22	44.42 ± 0.84	341.5 ± 6.5
6	14.02 ± 0.26	6.80 ± 0.12	2.90 ± 0.06	368.7 ± 6.26	1.90 ± 0.04	13.99 ± 0.26	31.18 ± 0.56	223.2 ± 2.9
7	6.45 ± 0.10	6.66 ± 0.16	3.24 ± 0.06	438.3 ± 1.76	1.66 ± 0.02	24.28 ± 0.10	36.98 ± 0.08	283.4 ± 2.3
8	10.40 ± 0.16	6.25 ± 0.06	7.34 ± 0.006	356.7 ± 8.24	1.38 ± 0.02	14.60 ± 0.20	16.25 ± 0.24	114.6 ± 1.1
9	18.68 ± 0.42	11.00 ± 0.34	6.48 ± 0.14	1091.4 ± 18.6	2.22 ± 0.02	31.22 ± 0.56	71.26 ± 1.06	357.4 ± 5.4
10	27.48 ± 0.60	15.62 ± 0.62	5.22 ± 0.16	819.8 ± 28.7	1.68 ± 0.04	30.52 ± 0.86	81.12 ± 1.46	225.0 ± 5.4
11	19.18 ± 0.34	6.82 ± 0.06	3.42 ± 0.06	418.4 ± 7.12	2.18 ± 0.04	30.98 ± 0.56	39.14 ± 0.58	197.9 ± 4.7
12	14.76 ± 1.24	145.88 ± 12.0	19.30 ± 1.44	3148.4 ± 114.1	8.11 ± 0.50	30.74 ± 1.96	95.71 ± 5.74	197.8 ± 12.5
In summer								
1	30.92 ± 1.12	10.04 ± 0.22	7.96 ± 0.22	874.1 ± 20.1	1.39 ± 0.04	45.22 ± 1.36	54.90 ± 1.40	168.4 ± 2.7
2	21.33 ± 0.44	7.62 ± 0.06	5.42 ± 0.04	598.7 ± 10.78	0.98 ± 0.01	26.92 ± 0.22	31.02 ± 0.32	73.78 ± 0.74
3	38.80 ± 0.28	5.90 ± 0.14	6.12 ± 0.08	539.0 ± 5.40	1.06 ± 0.01	24.66 ± 0.18	25.32 ± 0.18	43.33 ± 0.30
4	72.64 ± 0.66	7.74 ± 0.12	3.06 ± 0.04	162.6 ± 3.58	1.06 ± 0.02	38.04 ± 0.54	72.55 ± 1.24	141.5 ± 2.4
5	38.58 ± 0.96	6.02 ± 0.06	3.74 ± 0.06	271.3 ± 5.70	0.90 ± 0.02	17.42 ± 0.20	21.25 ± 0.46	72.42 ± 1.02
6	45.30 ± 0.36	4.50 ± 0.06	1.69 ± 0.02	135.9 ± 1.76	0.54 ± 0.01	19.34 ± 0.28	28.58 ± 0.32	95.62 ± 0.20
7	51.80 ± 0.56	5.42 ± 0.04	2.98 ± 0.04	167.6 ± 1.00	0.58 ± 0.02	20.74 ± 0.12	25.78 ± 0.02	93.80 ± 0.46
8	31.92 ± 0.32	5.94 ± 0.04	2.30 ± 0.04	141.2 ± 3.68	0.68 ± 0.01	18.28 ± 0.18	22.00 ± 0.28	88.22 ± 0.26
9	37.36 ± 0.86	4.98 ± 0.06	2.54 ± 0.04	177.9 ± 3.02	0.70 ± 0.02	20.26 ± 0.48	31.64 ± 0.28	115.9 ± 0.1
10	50.76 ± 0.96	3.54 ± 0.08	2.76 ± 0.06	210.9 ± 6.96	0.60 ± 0.02	19.10 ± 0.28	25.48 ± 0.48	94.48 ± 1.22
11	54.26 ± 0.98	5.18 ± 0.06	2.50 ± 0.04	191.9 ± 2.98	0.84 ± 0.02	17.38 ± 0.14	25.96 ± 0.46	72.74 ± 0.58
12	94.79 ± 3.50	9.34 ± 0.28	2.38 ± 0.04	198.6 ± 1.58	0.98 ± 0.02	23.68 ± 0.22	133.80 ± 0.48	133.8 ± 1.6

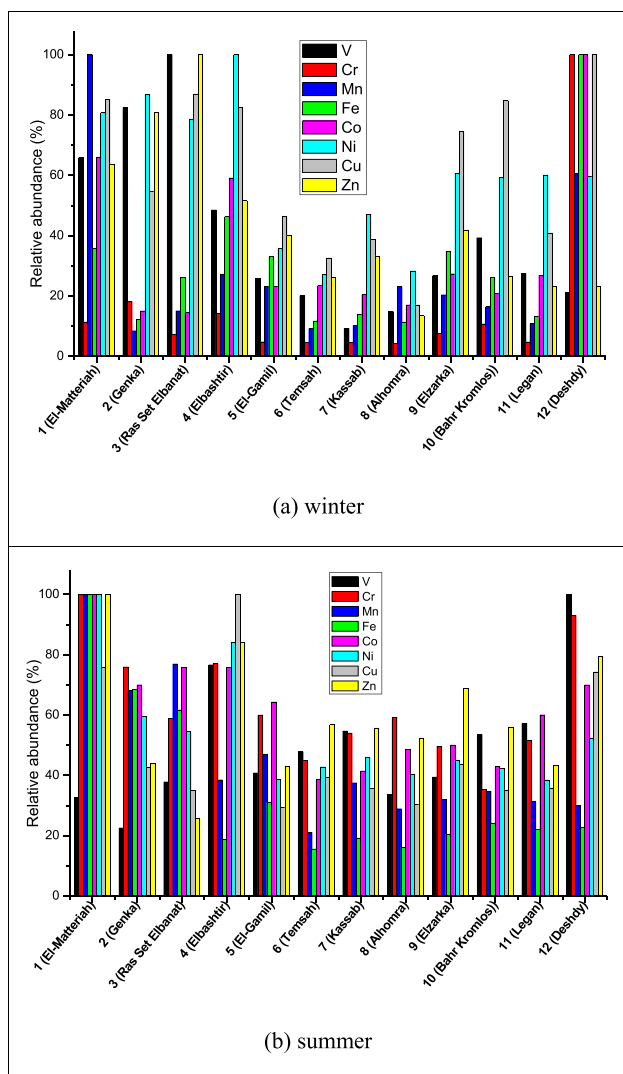


Fig. 2. Variation of metal ions in water samples of Lake Manzala. (a) winter and (b) summer.

3.2. Pollution assessment

Table 5 shows the EFs of the studied metal ions in sediment, compared with iron, the chosen immobile metal. All metals were more abundant than iron, with average metal EFs of 1.3–3.7 across the lake sites. The EFs increased in the following order: $Cr < V < Ni = Zn < Co < Mn < Cu$. Additionally, the average EFs for the site were within the range of 1.8–3.7 and increased in the following order: $(1) = (3) = (6) = (8) <$

$(12) < (7) < (5) = (9) < (10) < (11) < (2) < (4)$. The maximum EF was 8.3 for Cu and Zn at site (4), whereas the lowest EF was 0.8 for Cr at sites (9) and (11).

The geoaccumulation indices of the studied metal ions in the sediments of Lake Manzala are presented in Table 6. The I_{geo} values were mostly below zero and the mean I_{geo} values at the sites exceeded one at only sites (1), (2), (4) and (12). Additionally, the metal geoaccumulation indices were all less than zero except for those of Cu and Mn.

Table 7 shows the contamination risk indices for the metal ions studied in the sediments of Lake Manzala compared with the pristine background contents in sediments from the coastal Damietta region of the Mediterranean Sea [26, 27] and the Nile River in Damietta. The metal potential risk factors (E_r^I) relative to the sediments from the Damietta coast for V, Cr, Mn, Fe, Co, Ni, Cu and Zn were 0.1–0.9, 0.2–5.5, 0.6–3.0, 0.4–2.1, 2.2–14.1, 1.9–12.1, 5.0–76.0 and 0.4–14.0, with average values of 0.4, 1.0, 1.8, 1.1, 6.7, 6.1, 19.5 and 2.5, respectively. The average E_r^I values of sites (1)–(12) were 7.6, 9.0, 1.4, 15.6, 3.0, 1.9, 2.9, 3.1, 1.9, 4.0, 1.9 and 6.1, respectively. The RI and PLI ranged from 11.38 and 0.4 at site (3) to 124.9 and 2.9 at site (4), with mean values of 39.0 and 1.1, respectively. The potential risk factors E_r^I of V, Cr, Mn, Fe, Co, Ni, Cu and Zn were 0.4–3.4, 0.6–17.6, 0.5–2.4, 1.0–5.2, 1.1–7.2, 2.8–17.6, 3.9–58.5 and 0.3–8.5, relative to the sediments from the Damietta Nile River. The metal mean values were 1.4, 3.2, 1.4, 2.6, 3.4, 8.9, 15.0 and 1.5, respectively. The mean E_r^I values of sites 1–12 were 7.2, 8.4, 1.4, 14.8, 3.0, 1.9, 2.9, 3.1, 1.9, 4.0, 1.9 and 5.8, respectively. The RI and PLI ranged from 11.2 and 0.5 at site (3) to 118.4 and 3.8 at site (4), with mean values of 37.4 and 1.4, respectively. Relative to both background sites, the site risk indices increased in the following order: $(3) < (6) < (11) < (9) < (7) < (5) < (8) < (10) < (12) < (1) < (2) < (4)$.

The BAFs in WH are given in Table 8. All sites showed higher BAFs than one for the studied metal ions, with an average of 3.0. The average BAFs for each metal across the lake sites were 1.9–5.2 and increased in the following order: $Zn < Cu < Ni < V < Co < Cr < Fe < Mn$. Additionally, the average BAFs of the metals at each site were 2.2–3.3 and increased in the following order: $(12) < (1) < (9) < (5) < (8) < (10) < (3) < (7) < (2) < (4) < (6) < (11)$. The maximum BAF was 6.2 for Mn at site (11), whereas the lowest value was 1.6 for Zn at sites (2) and (5) and for Co at site (12).

3.3. Statistical correlations

Pearson's correlation analysis was carried out with the essential heavy metal contents and physicochemical parameters [10] in the aquatic ecosystem of Lake Manzala during winter (S3). Matrix analysis showed highly significant positive correlations ($P \leq 0.01$) of the V concentration in water with the Ni and Zn concentration in water, the biological oxygen demand (BOD), and the Zn concentration in WH; the Cr concentration with the Fe and Co concentrations in water; the Mn concentration with the Co concentration in water; the Fe concentration with the Co and Cu concentrations in water; the Co concentration with the Fe concentration

Table 2
Concentrations ($\mu\text{g g}^{-1}$) of essential heavy metals in sediments of Lake Manzala.

Site	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1	72.67 $\pm$ 1.45	44.32 $\pm$ 0.75	755.5 $\pm$ 18.9	27604 $\pm$ 524	23.28 $\pm$ 0.33	53.0 $\pm$ 0.90	46.83 $\pm$ 0.37	63.66 $\pm$ 0.32
2	83.57 $\pm$ 1.67	67.09 $\pm$ 1.07	1036 $\pm$ 9.33	21733 $\pm$ 282	20.20 $\pm$ 0.01	52.36 $\pm$ 0.63	64.98 $\pm$ 0.45	94.5 $\pm$ 0.57
3	13.62 $\pm$ 0.42	12.34 $\pm$ 0.21	233.0 $\pm$ 1.40	560.2 $\pm$ 5.04	3.55 $\pm$ 0.06	10.01 $\pm$ 0.02	8.49 $\pm$ 0.01	18.71 $\pm$ 0.11
4	107.9 $\pm$ 1.83	227.5 $\pm$ 2.96	527.1 $\pm$ 5.80	28043 $\pm$ 252	21.34 $\pm$ 0.30	62.73 $\pm$ 0.63	128.63 $\pm$ 1.16	310.0 $\pm$ 1.86
5	35.21 $\pm$ 0.28	20.35 $\pm$ 0.16	859.7 $\pm$ 2.58	10792 $\pm$ 64.8	7.58 $\pm$ 0.04	24.65 $\pm$ 0.20	17.17 $\pm$ 0.05	22.01 $\pm$ 0.15
6	18.38 $\pm$ 0.03	10.74 $\pm$ 0.09	261.1 $\pm$ 1.31	6802 $\pm$ 34.0	4.97 $\pm$ 0.02	18.08 $\pm$ 0.34	10.26 $\pm$ 0.04	15.69 $\pm$ 0.02
7	29.58 $\pm$ 0.41	17.18 $\pm$ 0.26	769.4 $\pm$ 7.69	10210 $\pm$ 102	6.98 $\pm$ 0.04	25.04 $\pm$ 0.23	16.37 $\pm$ 0.05	17.4 $\pm$ 0.12
8	36.30 $\pm$ 0.58	18.77 $\pm$ 0.11	598.7 $\pm$ 7.2	11802 $\pm$ 83	8.16 $\pm$ 0.07	25.71 $\pm$ 0.36	18.26 $\pm$ 0.11	20.03 $\pm$ 0.20
9	22.46 $\pm$ 0.20	8.95 $\pm$ 0.10	398.4 $\pm$ 1.20	6284 $\pm$ 31	5.06 $\pm$ 0.04	19.09 $\pm$ 0.36	10.64 $\pm$ 0.05	9.83 $\pm$ 0.06
10	47.26 $\pm$ 0.76	24.87 $\pm$ 0.25	1152 $\pm$ 3	12259 $\pm$ 37	9.61 $\pm$ 0.11	32.60 $\pm$ 0.39	23.37 $\pm$ 0.14	28.87 $\pm$ 0.06
11	18.36 $\pm$ 0.22	7.98 $\pm$ 0.08	580.5 $\pm$ 5.2	5504 $\pm$ 77	5.21 $\pm$ 0.03	18.89 $\pm$ 0.49	9.95 $\pm$ 0.10	9.21 $\pm$ 0.17
12	65.38 $\pm$ 1.18	34.74 $\pm$ 0.73	843.3 $\pm$ 10.1	21181 $\pm$ 169	17.01 $\pm$ 0.17	38.67 $\pm$ 0.39	40.38 $\pm$ 0.32	49.28 $\pm$ 0.70

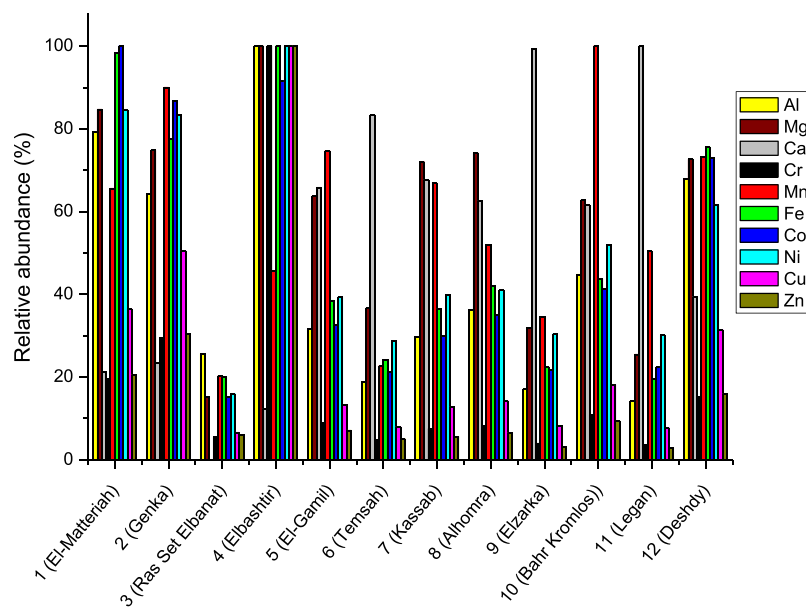


Fig. 3. Relative abundance of metal ions in sediments of Lake Manzala.

Table 3

Concentrations ($\mu\text{g g}^{-1}$) of essential heavy metals in WH of Lake Manzala.

Site	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1	13.070 $\pm$ 0.349	12.859 $\pm$ 0.125	410.546 $\pm$ 2.712	1763.724 $\pm$ 27.269	2.724 $\pm$ 0.022	21.320 $\pm$ 0.276	19.167 $\pm$ 0.256	53.587 $\pm$ 1.449
2	31.796 $\pm$ 1.088	13.543 $\pm$ 0.256	2792.040 $\pm$ 17.048	2065.353 $\pm$ 16.921	3.355 $\pm$ 0.045	13.837 $\pm$ 0.162	17.183 $\pm$ 0.196	29.379 $\pm$ 0.575
3	12.987 $\pm$ 0.279	31.365 $\pm$ 0.290	1302.138 $\pm$ 7.253	824.574 $\pm$ 10.388	1.864 $\pm$ 0.053	17.478 $\pm$ 0.487	24.192 $\pm$ 0.725	41.960 $\pm$ 1.025
4	37.954 $\pm$ 1.322	68.704 $\pm$ 1.50	365.510 $\pm$ 2.455	6483.344 $\pm$ 37.375	8.591 $\pm$ 0.021	22.989 $\pm$ 0.243	39.742 $\pm$ 0.694	51.900 $\pm$ 0.867
5	19.151 $\pm$ 0.510	8.458 $\pm$ 0.190	538.407 $\pm$ 14.853	504.757 $\pm$ 3.829	0.799 $\pm$ 0.005	7.303 $\pm$ 0.111	20.817 $\pm$ 0.694	12.403 $\pm$ 0.186
6	13.447 $\pm$ 0.329	10.039 $\pm$ 0.221	3299.451 $\pm$ 61.226	1445.155 $\pm$ 14.216	1.989 $\pm$ 0.034	8.825 $\pm$ 0.063	18.903 $\pm$ 0.280	15.332 $\pm$ 0.074
7	13.723 $\pm$ 0.27301	7.753 $\pm$ 0.177	2656.085 $\pm$ 45.780	481.223 $\pm$ 3.631	0.792 $\pm$ 0.014	9.273 $\pm$ 0.180	16.027 $\pm$ 0.208	12.726 $\pm$ 0.071
8	8.752 $\pm$ 0.135	6.030 $\pm$ 0.082	445.403 $\pm$ 8.212	296.184 $\pm$ 2.537	0.350 $\pm$ 0.003	4.955 $\pm$ 0.067	17.959 $\pm$ 0.069	11.703 $\pm$ 0.087
9	13.114 $\pm$ 0.645	24.523 $\pm$ 1.127	845.865 $\pm$ 36.949	407.623 $\pm$ 16.608	0.569 $\pm$ 0.018	5.744 $\pm$ 0.242	16.533 $\pm$ 0.646	17.905 $\pm$ 0.642
10	12.206 $\pm$ 0.464	11.083 $\pm$ 0.173	1492.335 $\pm$ 33.255	722.824 $\pm$ 10.407	1.241 $\pm$ 0.011	28.101 $\pm$ 0.064	41.591 $\pm$ 0.201	23.292 $\pm$ 0.280
11	22.712 $\pm$ 0.6421	12.386 $\pm$ 0.236	5606.795 $\pm$ 125.979	2325.562 $\pm$ 36.949	3.806 $\pm$ 0.048	17.146 $\pm$ 0.271	13.652 $\pm$ 0.063	21.884 $\pm$ 0.062
12	0.846 $\pm$ 0.019	6.856 $\pm$ 0.074	201.443 $\pm$ 1.595	338.518 $\pm$ 4.837	0.310 $\pm$ 0.004	7.690 $\pm$ 0.090	11.041 $\pm$ 0.037	18.659 $\pm$ 0.038

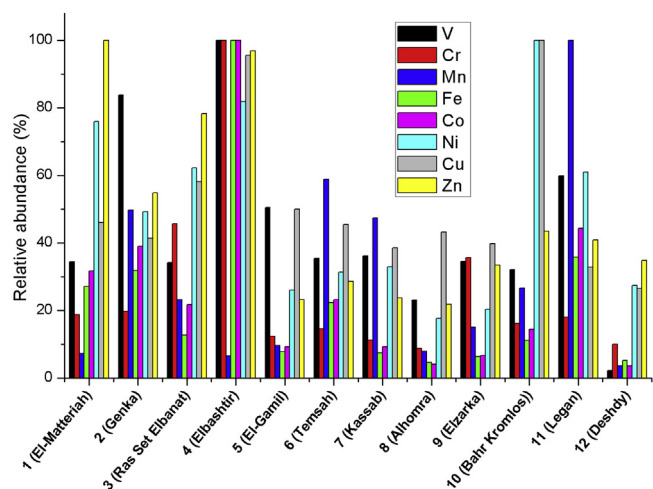


Fig. 4. Relative abundance of metal ions in water hyacinth of Lake Manzala.

in water; the Ni concentration with the BOD in water, and the Cu concentration in sediment; and the Cu concentration with the Fe concentration in water; and the Zn concentration with the BOD in water.

In sediments, highly significant correlations were found for V vs. Cr,

Table 4

Concentrations ($\mu\text{g g}^{-1}$) of heavy metals in Tilapia (wet weight) of Lake Manzala.

Metal	Gills		Muscles	
	Site 8	Site 10	Site 8	Site 10
V	11.744 $\pm$ 0.928	9.242 $\pm$ 0.148	2.533 $\pm$ 0.081	0.504 $\pm$ 0.021
Cr	0.329 $\pm$ 0.009	0.293 $\pm$ 0.013	0.282 $\pm$ 0.006	0.030 $\pm$ 0.006
Mn	8.436 $\pm$ 0.093	52.221 $\pm$ 0.418	0.876 $\pm$ 0.019	0.543 $\pm$ 0.044
Fe	155.749 $\pm$ 0.779	124.567 $\pm$ 0.872	23.816 $\pm$ 0.453	2.398 $\pm$ 0.078
Co	0.413 $\pm$ 0.004	0.112 $\pm$ 0.001	0.138 $\pm$ 0.004	0.006 $\pm$ 0.001
Ni	0.463 $\pm$ 0.005	0.420 $\pm$ 0.007	0.197 $\pm$ 0.004	0.029 $\pm$ 0.003
Cu	0.563 $\pm$ 0.004	0.839 $\pm$ 0.008	0.477 $\pm$ 0.010	0.054 $\pm$ 0.003
Zn	9.207 $\pm$ 0.074	11.547 $\pm$ 0.092	4.578 $\pm$ 0.060	0.957 $\pm$ 0.070

Fe, Co, Ni, Cu and Zn in sediment; Cr vs. Fe, Ni, Cu and Zn in sediment and V, Cr, Fe and Co in WH; Fe vs. Co, Ni, Cu and Zn in sediment; Co vs. Ni, and Cu in sediment; Ni vs. Cu and Zn in sediment; and Cu vs. Zn in sediment and Cr, Fe and Co in WH.

Finally, in WH, similar correlations were found for the V vs. PO_4 concentration in water, and Fe and Co in WH; Cr vs. PO_4 in water and Fe and Co in WH; Fe vs. PO_4 in water, and Co in WH; Co vs. PO_4 in water; Ni vs. Cu in WH; and Zn vs. the BOD in water.

Additionally, significant positive correlations ($0.01 < P < 0.05$) were found for Mn in water vs. Fe and Co in sediment; Co in water vs. Cu in water and Fe and Co in sediment; Ni in water vs. PO_4 , Cu and Zn in water;

Table 5

Enrichment factor of the studied metal ions in sediments of Lake Manzala.

Site	EF								Average
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
1	1.4	0.9	1.4	1.0	2.5	2.1	3.1	1.7	1.8
2	2.0	1.7	2.4	1.0	2.7	2.6	5.4	3.3	2.6
3	1.3	1.2	2.1	1.0	1.8	1.9	2.7	2.5	1.8
4	2.0	4.4	0.9	1.0	2.2	2.4	8.3	8.3	3.7
5	1.7	1.0	4.0	1.0	2.0	2.4	2.9	1.5	2.1
6	1.4	0.9	1.9	1.0	2.1	2.9	2.7	1.7	1.8
7	1.5	0.9	3.8	1.0	2.0	2.6	2.9	1.3	2.0
8	1.6	0.9	2.6	1.0	2.0	2.3	2.8	1.3	1.8
9	1.9	0.8	3.2	1.0	2.3	3.3	3.0	1.2	2.1
10	2.0	1.1	4.7	1.0	2.3	2.9	3.4	1.8	2.4
11	1.7	0.8	5.3	1.0	2.8	3.7	3.3	1.3	2.5
12	1.6	0.9	2.0	1.0	2.3	2.0	3.4	1.8	1.9
Average	1.7	1.3	2.9	1.0	2.3	2.6	3.7	2.3	2.2

Table 8

Log BAF of the studied metal ions in Lake Manzala in winter, 2015.

Site	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Average
1	2.5	2.9	4.1	3.2	2.7	2.7	2.4	2.0	2.8
2	2.7	2.7	6.0	3.7	3.4	2.5	2.5	1.6	3.1
3	2.3	3.5	5.4	3.0	3.2	2.6	2.5	1.7	3.0
4	3.1	3.5	4.6	3.6	3.3	2.6	2.7	2.1	3.2
5	3.0	3.1	4.9	2.7	2.6	2.6	2.7	1.6	2.9
6	3.0	3.2	6.1	3.6	3.0	2.8	2.8	1.8	3.3
7	3.3	3.1	5.9	3.0	2.7	2.6	2.6	1.7	3.1
8	2.9	3.0	4.8	2.9	2.4	2.5	3.0	2.0	2.9
9	2.9	3.3	5.1	2.6	2.4	2.3	2.4	1.7	2.8
10	2.1	2.9	5.5	2.9	2.9	3.0	2.7	2.0	3.0
11	3.1	3.3	6.2	3.7	3.2	2.7	2.5	2.0	3.3
12	1.8	1.7	4.0	2.0	1.6	2.4	2.1	2.0	2.2
average	2.8	3.0	5.2	3.1	2.8	2.6	2.6	1.9	3.0

Table 6

Geo-accumulation indices of the studied metal ions in sediments of Lake Manzala.

Site	I _{geo}								Average
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
1	-2.4	-1.5	0.4	0.5	0.9	0.4	1.9	0.9	0.14
2	-2.2	-0.9	0.9	0.1	0.7	0.4	2.4	1.5	0.36
3	-4.8	-3.3	-1.3	-1.8	-1.8	-2.0	-0.6	-0.8	-2.05
4	-1.8	0.9	-0.1	0.5	0.8	0.7	3.3	3.2	0.94
5	-3.4	-2.6	0.6	-0.9	-0.7	-0.7	0.4	-0.6	-0.99
6	-4.4	-3.5	-1.1	-1.5	-1.3	-1.1	-0.3	-1.1	-1.79
7	-3.7	-2.9	0.4	-1.0	-0.8	-0.6	0.4	-0.9	-1.14
8	-3.4	-2.7	0.1	-0.8	-0.6	-0.6	0.5	-0.7	-1.02
9	-4.1	-3.8	-0.5	-1.7	-1.3	-1.0	-0.3	-1.8	-1.81
10	-3.0	-2.3	1.0	-0.7	-0.4	-0.3	0.9	-0.2	-0.63
11	-4.4	-4.0	0.0	-1.9	-1.2	-1.0	-0.4	-1.9	-1.85
12	-2.5	-1.8	0.6	0.1	0.5	0.0	1.7	0.6	-0.10
Average	-3.34	-2.37	0.08	-0.76	-0.43	-0.48	0.83	-0.15	-0.83

Table 7

Risk contamination evaluation of the studied metals in Lake Manzala.

Comparison with sea sediment at Damietta										
Site	Site contamination factor QUOTE $E_r^i \cdot E_r^i$ in winter								RI	PLI
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		
1	0.6	1.1	2.0	2.1	14.1	10.2	27.7	2.9	60.61	1.7
2	0.7	1.6	2.7	1.6	12.3	10.1	38.4	4.3	71.67	1.9
3	0.1	0.3	0.6	0.4	2.2	1.9	5.0	0.8	11.38	0.4
4	0.9	5.5	1.4	2.1	12.9	12.1	76.0	14.0	124.90	2.9
5	0.3	0.5	2.3	0.8	4.6	4.8	10.1	1.0	24.34	0.8
6	0.1	0.3	0.7	0.5	3.0	3.5	6.1	0.7	14.88	0.4
7	0.2	0.4	2.0	0.8	4.2	4.8	9.7	0.8	22.96	0.7
8	0.3	0.5	1.6	0.9	5.0	5.0	10.8	0.9	24.81	0.7
9	0.2	0.2	1.0	0.5	3.1	3.7	6.3	0.4	15.40	0.4
10	0.4	0.6	3.0	0.9	5.8	6.3	13.8	1.3	32.16	1.0
11	0.1	0.2	1.5	0.4	3.2	3.6	5.9	0.4	15.38	0.4
12	0.5	0.8	2.2	1.6	10.3	7.5	23.9	2.2	49.04	1.4

Comparison with Nile sediment at Damietta										
Site	Site contamination factor QUOTE $E_r^i \cdot E_r^i$ in winter								RI	PLI
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		
1	2.3	3.4	1.6	5.1	7.2	14.9	21.3	1.7	57.5	2.2
2	2.6	5.2	2.2	4.0	6.2	14.7	29.5	2.6	67.1	2.5
3	0.4	1.0	0.5	1.0	1.1	2.8	3.9	0.5	11.2	0.5
4	3.4	17.6	1.1	5.2	6.6	17.6	58.5	8.4	118.4	3.8
5	1.1	1.6	1.8	2.0	2.3	6.9	7.8	0.6	24.2	1.0
6	0.6	0.8	0.5	1.3	1.5	5.1	4.7	0.4	14.9	0.6
7	0.9	1.3	1.6	1.9	2.2	7.0	7.4	0.5	22.9	0.9
8	1.1	1.4	1.3	2.2	2.5	7.2	8.3	0.5	24.6	1.0
9	0.7	0.7	0.8	1.2	1.6	5.4	4.8	0.3	15.4	0.6
10	1.5	1.9	2.4	2.3	3.0	9.2	10.6	0.8	31.6	1.3
11	0.6	0.6	1.2	1.0	1.6	5.3	4.5	0.3	15.1	0.6
12	2.0	2.7	1.8	3.9	5.3	10.9	18.4	1.3	46.3	1.8

Ni in water vs. V, Cr, Fe, Co, Ni and Zn in sediment and Cr, Fe, Co, and Ni in WH; Cu in water vs. Zn in WH; Zn in water vs. Zn in WH; V in sediment vs. PO_4 and Fe in water, Co and Zn in WH; Cr in sediment vs. Co in sediment and Zn in WH; Fe in sediment vs. Zn in WH; Co in sediment vs. Zn in sediment and Zn in WH; Ni in sediment vs. PO_4 , Fe and Co in WH; Cu in sediment vs. the dissolved oxygen (DO), V and Zn in WH; Zn in sediment vs. V and Zn in WH; Zn in sediment vs. Zn in WH; V in WH vs. Cr in WH; Cr in WH vs. Cu and Zn in WH; Fe in WH vs. Zn in WH; Co in WH vs. Zn in WH; and Ni in WH vs. Zn in WH.

In contrast, there were highly significant negative correlations for V vs. DO in water; Ni vs. DO and salinity in water; Cu vs. the salinity in water; Ni in WH vs. the BOD in water; and Zn in WH vs. DO in water. Additionally, significant negative correlations ($0.01 < P < 0.05$) were found for DO in water vs. Zn in water, V, Cr, Fe, Co, Ni, Cu and Zn in sediment, and V, Fe, Co and Cu in WH; and salinity in water vs. Ni and Zn in WH.

4. Discussion

4.1. Water

The relatively high levels of heavy metals in water samples from the eastern and southeastern sites, (1)–(4) and (12) (Table 1), were probably due to the presence of these metals in nearby drains, such as Ramsis, Hadus, El Mattariya and Bahr El Baqur. The low metal concentrations in the northern area were due to the exchange of the lake water with seawater inflows, which was more effective in the winter due to the annual withdrawal of freshwater [11]. Additionally, the higher concentrations of the studied metal ions, except for V, in winter than in summer was a result of the same process. The main drains contributing to the pollution of Lake Manzala were reported to be Bahr El Baqur, Hadous, Al Serw and Faraskaur, which are located in the eastern and southeastern regions [31]. Approximately $3.745 \times 10^9 \text{ m}^3$ of wastewater is usually discharged yearly into the lake. It was reported that as much as 9700 tonnes and 82.2 tonnes of oxygen are consumed in biological and chemical processes, respectively, in the lake per year, and 89700 tonnes of particulates, 7.4 tonnes of phosphate and 45 tonnes of petroleum hydrocarbons are annually discharged into the lake [32].

Comparison of the average concentrations of these metals with those reported for Lake Manzala [33] and the Nile River [34] (Table S4) revealed lower or comparable concentrations of the studied metals except for Cr and Ni, which were higher especially in the winter. However, the metal concentrations were remarkably higher than the values reported in nearby seawater such as in the Mediterranean Sea [35] and Suez Bay [36] or in open seawater such as that off the British coast [37] and in the Atlantic Ocean [37]. In addition, the detected metal concentrations mostly fell in Class II in the summer and Class III in the winter according to the classification suggested by the United Nations Economic Commission for Europe (UNECE) [5]. However, the concentrations of the metals complied with the UPLs for waste-receiving freshwater of Egyptian Law 48/1982, and the US EPA [38] the Netherlands [39] and the USA [20].

4.2. Sediments

Heavy metals are rapidly immobilized from water to the sediments, resulting in high concentrations of these pollutants in the matrix [40]. Sediment composition is therefore considered a good indicator of pollution in the water column, as sediments tends to concentrate heavy metals and other organic pollutants [41]. The location of the maximum values of most of the investigated metals V, Cr, Fe, Ni, Cu and Zn, at site (4) indicated that the Bahr El Baqur drain is the main source of metals immobilized in the sediment of Lake Manzala. The Ramsis, Hadus and El Mattered drains are the next largest heavy metal sources.

Comparison of the detected heavy metal concentrations in the sediments of Lake Manzala with reported values [9] (Table S5) showed a noticeable reduction in the metal concentrations and thus a decrease in

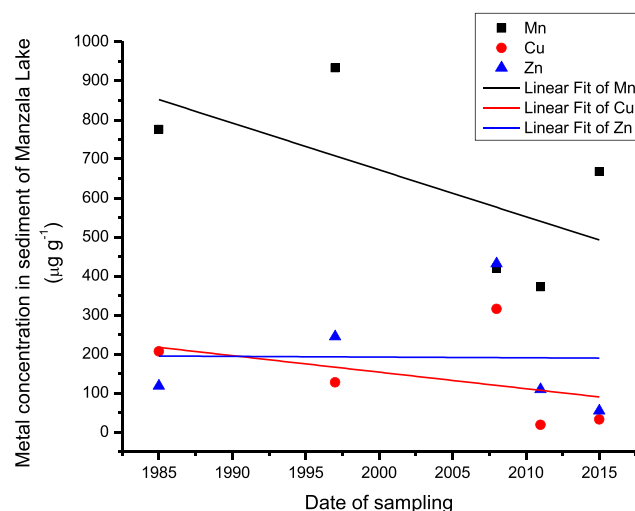


Fig. 5. Variation of metal concentrations in sediments of Lake Manzala during 1985–2015.

the pollution risk from 1985 – 2015, as shown in Fig. (5). This trend may be due to increased efforts to address water treatment and pollution control in Lake Manzala. The concentrations of the investigated metals were lower than those reported for Lake Burullus [42] but higher than those reported for Lake Nasser [43], the Mediterranean [44] and Red seas [45], the Suez Bay [46], and the British coast [37]. These results may indicate that Lake Manzala sediments are moderately affected by waste inflows.

4.3. Water hyacinth

The contents of heavy metals in aquatic plants are important indicators of their bioaccumulation and thus their danger to aquatic life as well as humans [47]. The maximum levels of the studied metal ions in WH leaves were detected at sites (4) (10) and (1), similar to the pattern of sediment metal-enrichment behavior. These results indicate that the accumulation of heavy metals in plants and sediments depends on their concentrations in water. This conclusion may be confirmed from 1) the relative similarity of the order of decreasing metal concentrations in WH, sediments and water and 2) the highest heavy metal concentrations were detected for Mn, Fe and Zn.

The metal concentrations in WH in the present study were mostly higher than the values reported previously in the same or other region, as detailed in Table (S6). This was probably due to the annual water withdrawal and the accumulation of heavy metals in WH during its transfer along the polluted drains, in contrast to sediments, which receive local pollutants exclusively [48].

4.4. Fish

The fish samples showed comparable heavy metal accumulation to that observed in the other studied ecosystem compartments. Fe, Mn and Zn were the most accumulated metals, followed by V. This may indicate that the enrichment of biota with heavy metals was influenced by the metal concentrations in water, sediments and plants. However, despite the observed dependence of the site heavy metal content on that in the ecosystem, a similar relationship could not be established in fish samples caught at sites (8) and (10), representing clean and polluted sites, respectively. Samples from both sites showed similar summation of metal contents of 13.738 and $12.735 \mu\text{g g}^{-1}$, respectively. These results may be due to the dynamic properties of Lake Manzala and the mobility of fish [49]. A remarkably large difference in the metal concentrations in gills compared with those in muscles is usually reported suggesting that muscles are safer for consumption [50].

The average metal concentrations in fish (*O. niloticus*) were comparable to the reported values in Lake Manzala, the Nile River, Malaysia and India as detailed in Table (S7).

The UPLs and permissible daily nutritional values (PNV) were calculated using the equations shown in (S8). The PNVs were significantly lower than the corresponding UPLs in the fish muscle. This results mean that tilapia muscle is safe for consumption.

4.5. Statistical correlation

The statistical correlation study revealed interesting features among the investigated metal concentrations in the aquatic ecosystem of Lake Manzala. The significant correlations among V, Ni and Zn in water indicated that they were mainly discharged from the same source, likely the Hadus and Ramsis agricultural drains, as their highest concentrations were detected at sites (1)–(4) and (12). The agricultural origin of these studied metals was further evidenced by the highly significant correlation of the BOD with V, Ni and Zn in water. Similarly, Cr, Mn, Fe, Co and Cu were likely mainly discharged from the Bahr El Baqur, El-Gamaliyah and El-Matariyah drains as their highest concentrations were at sites (1), (4), and (12).

The observed negative correlations of Ni, Cu, and Zn in water with salinity indicated that the origin of these metals is not seawater, but freshwater inflows. In addition, the observed inverse correlations of Ni, Cu and Zn in WH with the salinity of water indicated that the source of their bioaccumulation was freshwater containing these heavy metals. Additionally, the high concentrations of major elements in saline water may remediate contaminated WH, as reported for *Spirodela polyrrhiza*-contaminated with Cd and Ni [51].

V in water showed synergistic accumulation with Zn in WH, whereas Ni and PO_4 concentrations in water showed synergistic immobilization with most of the metal ions especially Cr, Fe, Co, Ni and Zn, in WH. V, Cr and Fe showed mutual synergistic accumulation in WH, as did Ni and Cu. The DO had an antagonistic effect on the accumulation of metals in WH, as concluded from their significant negative correlations with this parameter.

4.6. Pollution assessment

EFs of <1, <3, 3–5, 5–10, 10–25, 25–50 or >50 indicate no, minor, moderate, moderate to severe, severe, very severe, or extremely severe enrichment, respectively [52]. Accordingly, Lake Manzala may be considered to have minor enrichment with the studied metals ($\text{EF} = 1\text{--}3$), except for Cu, Mn and Zn, which were observed to be moderately and moderately to severely enriched ($\text{EF} = 3\text{--}5$ and $5\text{--}10$, respectively). Additionally, sites (2) and (4) showed severe enrichment of Cu and Zn. Therefore, the anthropogenic activities can be observed to occur across the Lake Manzala mainly due to the Cu, Mn and Zn-loaded discharges from the eastern and southeastern drains.

The I_{geo} index was calculated to determine the metal contamination of Lake Manzala sediments [13]. This expression was proposed to calculate the metal concentrations in sediments by comparing the current concentrations with undisturbed or crustal sediment (control) concentrations chosen to be the Egyptian coast of Mediterranean Sea [26, 27]. The metal concentrations can be classified into seven categories: unpolluted (Class 0, $I_{\text{geo}} < 0$), unpolluted to moderately polluted (Class 1, $0 < I_{\text{geo}} < 1$), moderately polluted (Class 2, $1 < I_{\text{geo}} < 2$), moderately to strongly polluted (Class 3, $2 < I_{\text{geo}} < 3$), strongly polluted (Class 4, $3 < I_{\text{geo}} < 4$), strongly to very strongly polluted (Class 5, $4 < I_{\text{geo}} < 5$) and very strongly polluted (Class 6, $I_{\text{geo}} > 5$). The highest grade reflects an enrichment that is 100 times above the baseline. Accordingly, site (4) was considered strongly polluted with Cu and Zn (Class 4), while sites (1), (2) and (12) were moderately to strongly polluted with Cu (Class 2 or 3). All other sites were less polluted. These results are in accordance with the results obtained from the EF study. These findings highlight the importance of increasing pretreatment efforts in the eastern and

southeastern drains especially the Bahr El Baqur drain that showed the highest EF and I_{geo} indices.

The RI was presented by Hakanson [14] to assess the level of heavy metal pollution in the sediment, according to the metal toxicity and the environmental response. The comparison of the present results was performed with reported data of the Nile River [26, 27] and Mediterranean Sea [28, 29] sediments, which were considered not subjected to contaminations from waste discharges. The E_r^i results from both uncontaminated sediments groups were generally close despite the large salinity differences. The assessment of the contamination risk of the studied metals in Lake Manzala sediments indicated that they possessed low-risk metal and site contamination factors ($E_r^i < 40$), except for Cu at site (4), the factor of which fell in the moderate-risk category ($40 \leq E_r^i < 80$). These results are in accordance with the EF and I_{geo} results in respect to the contamination risk of Cu at site (4). Other highly accumulated metals in the sediments of Lake Manzala such as Mn and Zn according to their EF and I_{geo} indices were classified in the low-risk category by using the E_r^i index due to their low toxicity potential. Additionally, the RI could be used to comprehensively evaluate the ecological risk caused by toxic metals. The RIs of the investigated sites indicated that the sites posed low-risk ($\text{RI} < 110$), except for site (4), which posed moderate-risk ($110 \leq E_r^i < 200$). These results may be due to the presence of maximum values of most of the investigated metals, namely V, Cr, Fe, Ni, Cu and Zn, at site (4) that exceeds the natural concentrations of the chosen immobile reference metal Fe in earth crust [25].

The PLI represents the number of times by which the heavy metal concentration in the samples exceeds the background concentration, and gives a cumulative indication of the overall level of heavy metal toxicity at a specific site [15]. Overall, the PLI of the investigated sites revealed no pollution influence ($\text{PLI} < 1$), except for sites (1), (2), (4) (10) and (12), influenced by the polluted discharges from the eastern and southeastern drains, where the PLI values exceeded unity which confirms the EF and I_{geo} results.

The BAF refers to the efficiency of a plant species to absorb a metal into its tissue from the surrounding environment [53]. The highest bioaccumulation was found for Mn, Fe and Cr, and their preferred sorption may be the reason for the lowest BAF for Zn, Ni, and Cu [54]. Additionally, the highest average BAF values were recorded at sites (6) (11) and (4), which may be attributed to the eutrophication previously reported at these sites [10].

5. Conclusion

The determined pollution risk indices for heavy metals in Lake Manzala ecosystem indicated no risk of pollution with all the studied metals, except for Cu, Mn and Zn, for which moderate pollution were observed. Untreated or partially treated wastewater effluents from agricultural, domestic and industrial drains endanger the aquatic life in Lake Manzala. The effluents from drains located in the eastern and southeastern region of the Lake Manzala, in particular, are primarily responsible for the loads of the essential heavy metals. These polluted loads are transported via water streams and floating plants throughout the aquatic ecosystem. The ongoing important reclamation processes of the lake and the observed improvement in its water quality will be more effective with continuous removal of the floating plants such as WH, entering the lake. In addition, as the sediments of Lake Manzala have served as a pollutants sink for decades, agitating a large sediment area simultaneously or within a short period is not recommended. Additionally, wastewater effluents should be effectively treated prior to discharge into the lake.

Conserving biodiversity such as plants, migratory birds and other living organisms in lake ecosystems is mandatory. Although, the present study indicated that the metal concentrations in tilapia muscle were within the reported and permissible concentrations, clear instructions to avoid consuming tissues other than muscle may be necessary. Community awareness should be raised about the importance of the lake ecosystem.

Declarations

Author contribution statement

Randa Elmorsi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Khaled Abou-El-Sherbini: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mohamed Hamed: Conceived and designed the experiments.

Gamal Mostafa: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

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