Distribution and accumulation of heavy metals in Lake Manzala, Egypt

Raafat Mandour
Mansoura University, Mansoura, Egypt

ABSTRACT
Lake Manzala is the largest saline lake and the second largest one among all lakes in Egypt. Heavy metals' contamination is the most fundamental kind of contamination around the world, particularly in Lake Manzala. The purposes of this paper are investigating the relationship between contents of some heavy metals and major oxides of the Quaternary sediments of Lake Manzala islands as well as the correlation coefficient factor among them. Ten samples of both water and superficial bottom sediments had been representing the lake Manzala through summer, 2019 is covering the sources of pollution to carry out this study. Six heavy metals estimated to assess the environmental risk. The elements were analyzed through atomic absorption spectrometer. Concentration of heavy metals Fe > Zn > Pb; Fe > Mn > Zn > Pb > Cu > Cd in water and sediment is recorded within the southern and southeastern parts of the lake. Significant oxides' arrangement is SiO\(_2\) > MgO > CaO > Na\(_2\)O > Al\(_2\)O\(_3\) > K\(_2\)O > FeO\(_3\). Eco-toxicological of heavy metals' contamination was among the bottom sediments of Lake Manzala. Target hazard quotients (THQ) for individual metals are arranged within the order; Zn > Pb > Cu > Cd. Therefore, heavy metals should eliminate from the wastewater to protect the people and the environment.

Introduction

Millions of cubic meters of untreated domestic, industrial, and agricultural drainage waters are discharged annually into the lake [1]. These drains have an effect on the measure, and quality of the lake, threatens human health and cause a serious pollution problem.

These results led to the accumulation and distribution of contaminants like heavy metals within the lagoon sediments. Expected contamination of Lake Manzala with heavy metals has been reported [2]. Heavy metals include potentially toxic (Cd, Pb), probably essential and far from is essential (Cu, Zn, Fe, Mn) [3]. Häder et al. [4] declared provoking deleterious effects on environmental quality and ecosystem sustaina

bility with the aid of human intervention. The primary relationship studies between environmental healthy and therefore, the ecosystems functioning of Lake Manzala done by Orabi and Osman [5]. Due to multiple waste discharges, there has been a greater metal concentration at the eastern and southeastern sites of Lake Manzala than permissible limits [6]. Sediments are considered an indicator of the degree of heavy metal contamination in water environment [7]. The heavy metals of anthropogenic origin occur within the ecosystem naturally by litho-genie processes that have a tendency to be bio-available then grow to be toxic pollutants [8]. The aquaculture activities can effect by hydrological conditions of lake water and resulting in a decrease in fish productivity and lack of biodiversity [9].

CONTACT Raafat Mandour raafat_mandour@hotmail.com Mansoura University, Egypt

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The foremost aim of this research is to investigate the connection between the contents of some heavy metals and major oxides of the Quaternary sediments of Lake Manzala islands and coefficients of correlation factor among them.

**Materials and methods**

**Study area**

Lake Manzala is one of the three mains Nile Delta wetland ecosystems, Egypt, lies between latitude 31°10’–31°40’ N and longitude 31°50’–32°25’ E (Figure 1). It is rectangular and somewhat shallow with an average depth of about 100 cm.

**Hydro-chemistry**

The influx of water into Lake Manzala includes: the Mediterranean saline water, the occasional rainfall in winter, the surface brackish drainage water (agricultural, industrial, and domestic wastes) and therefore, the vertical seepage from the underlying groundwater, which exists under semi-confined conditions. Mandour [10] reported water chemistry of Lake Manzala area as:

Water chemical types: Chloride – Sodium
Hydro-chemical classification: (Cl – Na)
Hypothetical salt assemblage as group:
NaHCO$_3$, (Na +K) C I, Na$_2$SO$_4$, C a (HCO$_3$)$_2$, Mg (HCO$_3$)$_2$
Na$^+>$ Ca$^{++}>$ Mg$^{++}>$ K$^+$ – HCO$_3^->$ Cl$^->$ SO$_4^{--}$

**Sampling and technique of study**

The study was carried out on Lake Manzala through summer, 2019, to monitor and evaluate the levels of some heavy metals and major oxides in water and sediments. Ten samples of both water and superficial bottom sediments have been collected. The sample sites have

| Total dissolved salts (TDS) mg/l | Major cations | Major anions |
|-------------------------------|---------------|--------------|
|                               | K$^+$         | Na$^+$       | Mg$^{++}$    | Ca$^{++}$   | Cl$^-$ | SO$_4^{--}$ | HCO$_3^-$ |
| 2497.67                        | 17            | 721.97       | 42           | 50          | 591.7  | 294         | 781       |

*Figure 1. Location Map (Lake Manzala in the NE Nile Delta, Egypt).*
been chosen to cover sources of pollution near to discharges of most drains which consider the main source of pollution of the study area. Every one of the safeguards happened to limit dangers of the test tainting were followed during the assortment and treatment of tests. These samples have been chemically analyzed for the determination of their major oxides (Silica oxide SiO₂, Aluminum oxide Al₂O₃, Ferric oxide Fe₂O₃, Magnesium oxide MgO, Calcium oxide CaO, Sodium oxide Na₂O and Potassium oxide K₂O) and a few heavy metals (Cu, Zn, and Pb, Fe, Mn and Cd). The study used the standard of the American Public Health Association (APHA) [11] for the collection, preservation and digestion technique. Heavy metals concentrations were measured using a graphite furnace atomic absorption spectrometer (Buck Scientific Company, USA) after the digestion technique. Calibration standards and quality control samples have been prepared freshly daily. The reference standard materials used to assess the precision and accuracy of the procedure. The study used analytical grade chemicals of certified standard solutions for the aim of sample preparation and its analysis.

**Statistical analysis**

It had been finished for all samples using the Statistical Package for the Social Sciences (SPSS) software program for Window version 16 [12]. The concentration of heavy elements presented as a mean and standard deviation (SD). Pearson’s coefficient of correlation was calculated between different trace elements. For any of the used tests, results are considered as statistically significant if p-value ≤ 0.05, moderate significant ≤ 0.01, and highly significant ≤ 0.001.

**Results**

The concentrations of heavy metals in water samples and sediments of Lake Manzala were represented in Tables 1–2 and illustrated by graphs 1-2. Subsequent to the summarized study on the environmental status of studied heavy metals, which might cause risk on human health and environmental effects. Major oxides sequence is SiO₂ > MgO > CaO > Na₂O > Al₂O₃ > K₂O > Fe₂O₃ (Tables 3) and illustrated by graph (3). Average concentrations of heavy metals in water and sediment as compared with average EPA limits [13] have been; Fe > Mn > Zn > Pb > Cu > Cd (Table 4). Whereas, average concentrations of heavy metals of sediment samples in relation to sediment quality guidelines (SQGs) showed that Cd in sediments become rated non-polluted element. Sediment quality guidelines are unknown for Fe and Mn (Table 5). Pearson’s correlation coefficients (r) between concentrations of heavy metals in water and in sediment of Lake Manzala showed that a significant direct correlation between Cu in sediment and in water as

| Table 1. Concentrations of heavy metals (mg/l) in water samples of Lake Manzala. |
|---------------------------------|---|---|---|---|---|---|
| Sample no | Fe  | Mn  | Zn  | Pb  | Cu  | Cd  |
| 1          | 30.15 | 9.47 | 8.20 | 5.42 | 2.86 | 1.83 |
| 2          | 51.23 | 11.12 | 10.86 | 6.92 | 3.19 | 1.13 |
| 3          | 34.07 | 12.31 | 9.11 | 6.26 | 3.49 | 1.91 |
| 4          | 41.08 | 12.21 | 9.27 | 6.29 | 4.67 | 1.99 |
| 5          | 34.21 | 10.99 | 9.35 | 6.01 | 3.27 | 1.95 |
| 6          | 36.66 | 10.34 | 7.09 | 6.08 | 3.24 | 2.45 |
| 7          | 30.56 | 13.67 | 9.88 | 5.84 | 3.22 | 2.22 |
| 8          | 37.39 | 13.20 | 8.19 | 5.51 | 3.28 | 1.85 |
| 9          | 27.55 | 9.9   | 9.07 | 5.55 | 2.77 | 1.57 |
| 10         | 58.02 | 8.96 | 6.73 | 2.95 | 2.6  | 1.37 |

| Table 2. Concentrations of heavy metals (mg/g) in sediment samples of Lake Manzala. |
|---------------------------------|---|---|---|---|---|---|
| Sample no | Fe  | Mn  | Zn  | Pb  | Cu  | Cd  |
| 1          | 308.08 | 47.43 | 42.06 | 39.74 | 6.36 | 2.04 |
| 2          | 342.81 | 49.98 | 101.73 | 55.32 | 6.45 | 1.58 |
| 3          | 330.41 | 63.78 | 46.53 | 50.67 | 35.11 | 2.12 |
| 4          | 342.41 | 58.65 | 47.16 | 53.58 | 37.07 | 2.71 |
| 5          | 334.81 | 49.3  | 48.1  | 47.49 | 32.9  | 2.59 |
| 6          | 337.91 | 48.62 | 39.67 | 50.42 | 27.56 | 2.97 |
| 7          | 326.81 | 114.51 | 49.19 | 45.93 | 21.58 | 2.91 |
| 8          | 341.71 | 41.07 | 41.07 | 45.58 | 34.52 | 2.09 |
| 9          | 286.31 | 48.52 | 43.06 | 45.84 | 5.6  | 1.75 |
| 10         | 446.61 | 46.21 | 39.28 | 38   | 3.39 | 1.73 |
Zn with $P \leq 0.05$ (Table 6). Whereas, Pearson’s correlation coefficients ($r$) between percent (%) of major oxides and concentrations of heavy metals in water and in sediment of Lake Manzala showed that Fe, Mn, Pb and Cd haven’t any correlation with any of those major oxides (Table 7). The calculated values of THQ are employed to precise the potential risk indicate that anglers are under threat (1.01) than the overall population (0.41) (Table 8), the health risk is calculated supported data documented by Hammed et al. [14].

**Table 3.** Descriptive statistics for major oxides in Lake Manzala.

| Major oxides % | Sample no |
|----------------|-----------|
|                | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
| SiO$_2$        | 54.65 | 56.7 | 55.3 | 54.2 | 50.15 | 51.3 | 51.7 | 52.1 | 51 | 52.1 |
| Al$_2$O$_3$    | 8.08  | 7.8  | 8.5  | 8.05 | 7.6  | 8.8  | 7.8  | 8.6  | 8.3 | 8.4  |
| Fe$_2$O$_3$    | 0.35  | 1.05 | 1.4  | 0.78 | 1.65 | 1.75 | 1.8  | 1.75 | 1.85 | 1.8  |
| CaO            | 29.8  | 17.9 | 22   | 20.3 | 22.9 | 22.2 | 24.3 | 20.8 | 20.8 | 20.6 |
| MgO            | 37.8  | 33.4 | 29.7 | 22.6 | 30.3 | 31.4 | 29.5 | 30   | 29.7 | 28.5 |
| Na$_2$O        | 7.5   | 8    | 11.3 | 10.7 | 14.1 | 11.4 | 14.7 | 15.2 | 14.6 | 15.4 |
| K$_2$O         | 2.6   | 2.95 | 3.05 | 2.9  | 3.2  | 3.4  | 3.05 | 3.2  | 3.4  | 3.2  |

Mean ± SD

| Major oxides % | Mean ± SD |
|----------------|-----------|
| SiO$_2$        | 52.9 ± 2.1 |
| Al$_2$O$_3$    | 8.2 ± 0.4  |
| Fe$_2$O$_3$    | 1.4 ± 0.5  |
| CaO            | 22.2 ± 3.2 |
| MgO            | 30.3 ± 3.8 |
| Na$_2$O        | 12.3 ± 2.9 |
| K$_2$O         | 3.1 ± 0.2  |

**Table 4.** Average concentrations of analyzed heavy metals in water and sediment compared with average EPA [13] limits.

| Element | Heavy metals in water (n = 10) Mean ± SD | EPA [13] limits for water | Heavy metals in sediment (n = 10) Mean ± SD | EPA [13] limits for sediments |
|---------|------------------------------------------|---------------------------|---------------------------------------------|-----------------------------|
| Fe      | 38.1 ± 9.7                               | 300                       | 339.8 ± 41.6                               | 15                          |
| Mn      | 11.2 ± 1.6                               | -                         | 63.8 ± 26.4                                | -                           |
| Zn      | 8.8 ± 1.2                                | 5000                      | 49.8 ± 18.6                                | 123                         |
| Pb      | 5.7 ± 1.1                                | 50                        | 47.3 ± 5.5                                 | 10                          |
| Cu      | 3.3 ± 0.6                                | 50                        | 21.1 ± 14.1                                | 25                          |
| Cd      | 1.8 ± 0.4                                | 2.37                      | 2.3 ± 0.5                                  | 6                           |

Graph 1. Concentrations of heavy metals (mg/l) in water samples of Lake Manzala.
**Graph 2.** Concentrations of heavy metals (mg/g) in sediment samples of Lake Manzala.

**EPA [13] Environmental Protection Agency limit for water and sediments**

*a: not available data. SQG: sediment quality guidelines*

**The value of THQ**

Greater than 0.5, indicates high health risk
Lower than 0.5, indicates low health risk

**Discussion**

Metals generally enter the aquatic environment through erosion of the geological matrix, or due to anthropogenic activities caused by industrial effluents, domestic sewage [15]. The mean concentration of the measured metals in the water and sediments was found to within the following sequence; Fe > Zn > Pb; Fe > Mn > Zn > Pb > Cu > Cd, as compared to Environmental Protection Agency (EPA) [13]. Depending on the SQG of EPA, sediments were classified as: low polluted, moderately polluted and heavily polluted [16]. Manzala sediments are often categorized as moderately polluted with Pb (8), Cu (5), and Zn (1) using SQGs. Cadmium in sediments was rated non-polluted element (Table 5). During this investigation, the sediment quality guidelines (SQGs) developed for the aquatic ecosystem [17] became applied to estimate eco-toxicological sense of heavy metal

**Graph 3.** Major oxides %
Table 5. Average concentrations of analyzed heavy metals of sediment samples in relation to SQGs.

| Element | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | SQG low polluted | SQG moderate polluted | SQG heavily polluted |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------------------|----------------------|----------------------|
| Fe      | 308.08 | 342.81 | 330.41 | 342.41 | 334.81 | 337.91 | 326.81 | 341.71 | 286.31 | 446.61 | a                | a                    | a                    |
| Mn      | 47.43  | 49.98  | 63.78  | 58.65  | 49.3   | 48.62  | 114.51 | 41.07  | 8.52   | 46.21  | a                | a                    | a                    |
| Zn      | 42.06  | 101.73 | 46.53  | 47.16  | 48.1   | 39.67  | 49.19  | 41.07  | 43.06  | 39.28  | a                | a                    | a                    |
| Pb      | 39.74  | 55.32  | 50.67  | 53.58  | 47.49  | 50.42  | 45.93  | 45.58  | 45.84  | 38     | a                | a                    | 200-200               |
| Cu      | 6.36   | 6.45   | 35.11  | 37.07  | 32.9   | 27.56  | 21.58  | 34.52  | 5.6    | 3.39   | 90               | 90-200               | 60-60                |
| Cd      | 2.04   | 1.58   | 2.12   | 2.71   | 2.59   | 2.97   | 2.91   | 2.09   | 1.75   | 1.73   | 40               | 40-60                | 25-50                |

Therefore, an assessment of heavy metal contamination in sediment may be a crucial tool to assess the danger of the hydro-geochemical environment and to determine the distributions in sediments.

Table 7 indicates a significant correlation between A123 and Zn in water as MgO with Pb and Cu in water at P ≤ 0.05. Iron, Zn, Pb, Cu and Cd have no correlation with any of the major oxides in sediment. Bai et al. [20], having similar sources as estimated by Dan et al. [19], Table 7 indicates a significant correlation between A123 and Zn in water as MgO with Pb and Cu in water at P ≤ 0.05. Iron, Zn, Pb, Cu and Cd have no correlation with any of the major oxides in sediment. Bai et al. [20].
Table 6. Pearson’s correlation coefficients (r) between concentrations of analyzed heavy metals in water and in sediment of Lake Manzala.

| Heavy metals in sediment | Heavy metals in water |
|--------------------------|-----------------------|
| Fe                       | Mn                    | Zn | Pb | Cu | Cd |
| Fe                       | 0.87**                |    |    |    |    |
| Mn                       | 0.84**                | 0.72*|    |    |    |
| Zn                       |                       | 0.85**|    |    |    |
| Pb                       |                       |     | 0.73*|    |    |
| Cu                       |                       |     |     | 0.92***|    |
| Cd                       |                       |     |     |     | 0.92***|

*, **, *** significant correlation at $P \leq 0.05$, moderate significant $P \leq 0.01$, and highly significant $P \leq 0.001$

Table 7. Pearson’s correlation coefficients (r) between % of major oxides and concentrations of analyzed heavy metals in water and in sediment of Lake Manzala.

| Oxides | SiO2 | A12O3 | Fe2O3 | CaO in water | MgO | Na2O | K2O |
|--------|------|-------|-------|--------------|-----|------|-----|
| Fe     | 0.31 | 0.04  | 0.01  | -0.56        | -0.19| -0.03| -0.004|
| Mn     | 0.08 | -0.13 | 0.14  | -0.16        | -0.37| 0.19 | -0.06|
| Zn     | 0.4  | -0.72*| -0.23 | -0.22        | -0.02| -0.29| -0.3 |
| Pb     | 0.36 | -0.28 | -0.3  | -0.11        | 0.06 | -0.5 | -0.17|
| Cu     | 0.27 | -0.12 | -0.35 | -0.24        | -0.66*| -0.23| -0.24|
| Cd     | -0.43| 0.23  | 0.14  | 0.42         | -0.16| 0.13 | 0.15 |

In sediment

| Fe     | -0.02| 0.2  | 0.22  | -0.32        | -0.28 | 0.3 | 0.11 |
| Mn     | -0.16| 0.02 | 0.32  | 0.03         | -0.17 | 0.4 | 0.02 |
| Zn     | 0.06 | -0.48 | -0.26 | -0.45        | 0.22  | -0.5 | -0.26|
| Pb     | 0.39 | -0.14 | -0.12 | -0.56        | -0.31 | -0.37| 0.05 |
| Cu     | -0.14| 0.13 | 0.1   | -0.1         | -0.5  | 0.16 | 0.12 |
| Cd     | -0.41| -0.04| 0.12  | 0.26         | -0.3  | 0.12 | 0.11 |

*, **, *** significant correlation at $P \leq 0.05$, moderate significant $P \leq 0.01$, and highly significant $P \leq 0.001$

hence, the influence of anthropogenic sources cause different risk levels of various metals [25]. This through Tariq [26] who suggested that untreated wastewater have induced high gathering of heavy metals which may be providing wellness risk to the population. Green growth biomass is used for bio remediation of heavy metallic contaminated gushing by utilizing adsorption or via combination into the cells [27]. Likewise, incessant plant collection ought to be urged to assist with diminishing the relocation of heavy metals from the contaminated soils into the surrounding environment [28].

Conclusions

The above results confirmed that the lake is facing a serious threat of metal pollution. The main source for metal contamination in the wastewater effluents is via drains in southern and southeastern parts. To deteriorate the water quality aimed at a rise in accumulation of metals in fish tissues. Increasing awareness of pollution risk might support the implemented remediation programs to face the rapid deterioration regarding the importance of the lake ecosystem. Population awareness, especially anglers of health risk from the intake of the heavy metals through fish consumption. This paper provided
a framework for future research because of the presence of some heavy metals in the water and sediment of Lake Manzala also as possible eco-toxicological effects on the environment.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Raafat Mandour http://orcid.org/0000-0001-5052-5954

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Table 8. Estimated THQ for each metal from consumption of fish by the general population and anglers.

| THQ | Zn | Pb | Cu | Cd | Exposure group |
|-----|----|----|----|----|----------------|
| 1.01| 1.87| 1.21| 0.76| 0.21| Fishermen |
| 0.41| 0.94| 0.460| 0.17| 0.06| General Population |

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