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ORIGINAL ARTICLE

Spatial Distribution and Ecological Risk Assessment of Trace Metals in Surface Sediments of Lake Qarun Wetland, Egypt

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KEYWORDS

Qarun Lake;
Pollution indices;
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ABSTRACT: Wetlands sediments could be critical indicators to control contamination in the aquatic ecosystem. Qarun Lake is regarded as the third biggest lake in Egypt that is not related to any sea. Twelve georeferenced sediment samples were gathered in September, 2020 from the different locations. Five heavy metals (Pb, Cd, Cr, Ni, and Co) were measures in the sediments estimated by Atomic Absorption Spectrophotometer. Grain size and content of organic matters in the sediment were estimated on the basis of standard assays, as well as the contamination factor, geoaccumulation index, ecological risk factor, contamination degree and potential ecological risk index in the sediment. Data revealed that the average concentration could be arranged as Ni (27.36 mg k g^{-1}) > Pb (18.28 mg k g^{-1}) > Cr (15.31 mg k g^{-1}) > Co (11.16 mg k g^{-1}) > Cd (23.31 mg k g^{-1}). Cd, Co and Pb were estimated to be in the range of EU (2002) and the US EPA (1999), while Co and Ni in the range of EU (2002). The ecological risk index (Er) of the studied elements in sediments of lake could be arranged as: Ni > Pb > Co > Cd > Cr. In addition, the highest-integrated potential ecological risk was on the south side of the lake, which is subjected to huge amounts of drainage water composed of organic and inorganic pollutants.

INTRODUCTION

Wetlands sediments could be used as indicators for controling contaminants in the aquatic ecosystems. They are contaminating with many sources of harmful and toxic substances [1], like trace elements accumulation of sediments via several pathways [2]. Moreover, wetlands are productive environments, which provide many advantages. They are curdling of biodiversity enriching water and primary productivity for survival of several plants and animals. The interactions of wetlands constituents like water, plants and animals enable them to encounter many important functions [3].

The accumulation of trace elements is enhancing in enclosed and semi-enclosed inland lakes such as El-Temsah, El-Mora Qarun, and Wadi El-Rayan lakes, where exchanging of water with the open sea is limited or absent [4]. In addition, changes in evaporation and precipitation can affect the physical and chemical variables in the lakes [5, 6]. Some trace elements like Fe, Cu, and Zn, are crucial micronutrients needed for the growth and function of organisms, but exposure to higher concentrations from these elements could be detrimental, while Cd, Ni, Pb, and Sn, are regarded as toxic elements for human and aquatic organisms [7].

Qarun Lake is regarded as the third-largest lake in Egypt that is not related to any sea. It known nowadays Birket Qarun [8, 9]. It is subjected to huge levels of drainage

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water composed of organic and inorganic pollutants. Variability of nutrient concentrations is directly related to agricultural and industrial wastes thrown into the lake [10, 11]. Lake Qarun resembles 7.7% of fish production from Egyptian lakes [12]. Since 2011, higher degrees of fish organs deformation and discoloration, assumed to be the result of environmental pollutants affects the fishing community, both socially and economically. This study comprises some trace metals (Pb, Cd, Cr, Ni, and Co) that were analyzed in sediments collected from Qarun Lake for checking spatial distribution and potential influence on the environment.

MATERIALS AND METHODS

Study area

Qarun Lake occupies a characteristic location northwest of the Faiyum Oasis 83 km southwest of Cairo in the western desert. It is the third-huge lake in Egypt, located at longitudes of 30° 24' and 30° 49' E and latitudes of 29° 24' and 29° 33' N (Figure 1). It is a closed saline basin with rectangular shape of around 40 km length and 5.7 km width with water depthes ranges from 1 to 8 meters. It has a surface area of 215 km^2 and a water volume of 1,100,000000 m^3. The water level ranges from 43 to 45 meters below the sea level [13, 14].

It is surrounded from the south and east by urban and cultivated areas while from the north and west by unoccupied desert areas [14]. The lake and its surrounding area are a protected area and set as a Ramsar site since 2012. In prehistory, it was a freshwater lake, with an area vary between 1,270 km² (490 mi²) and 1,700 km² (656 mi²), while today persists as a smaller saltwater lake called Birket Qarun.

Environmental impact of Lagoon

Qarun Lake plays a significant role from the agriculture and ecologic point of view for the Faiyum region as it receives the drainage water from the irrigation canals. The lake's main sources of water are a mixture of untreated agriculture drainage and domestic wastewater (about 450 million m^3/year) from El-Faiyum province [15]. The drainage in El-Faiyum depression is affected by gravity, and composed of 3 major drains (El-Bats, El Mashroah, and El-Wadi), besides several small drains, which terminate into the lake.

The surrounding plants and fauna are also starting to disappear due to the increased salinity that is killing the entire area. The studied Lake salinity increased from 3.5 g l^{-1} in 1890 to 26 g l^{-1} in 1950 and reached nearly 50 g l^{-1} by 2010. Moreover studies conducted early in 1930 that the lake was converting to a saltwater lake from a freshwater lake, as a result of more intense irrigation agriculture [12, 15].

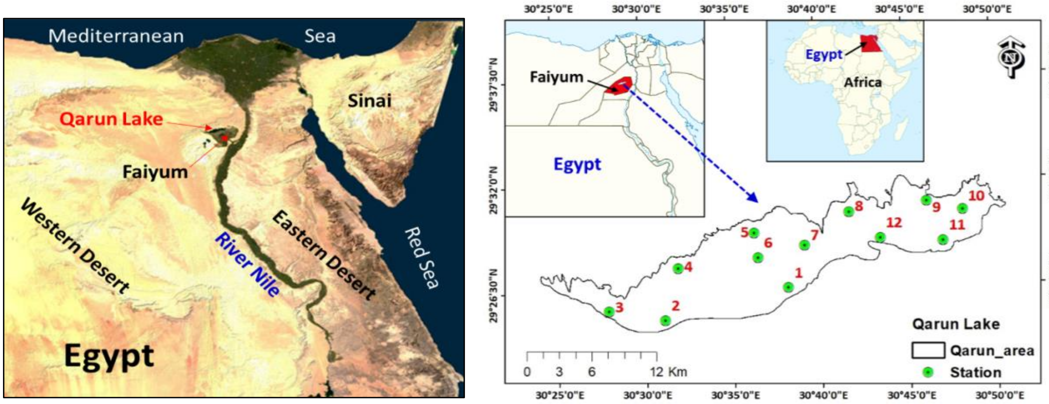

Figure 1. Map of Egypt showing location of Qarun Lake and map of sampling sites (1-12) in studied Lake.

Samples collection

Twelve sediment samples (1 kg) were gathered during September, 2020 from the several sites representative for the investigated Qarun Lake (Figure 1). Each location composed of a mixture of 3 samples from each location. Samples were stored using acid-rinsed polyethylene plastic bags, air-dried, well mixed, sieved using 2 mm sieves for removing gravels and debrises, and kept in plastic bags to be ready for analyses. The samples were stored frozen in sealed acid pre-cleaned plastic bags.

Samples treatment and analysis

Heavy metals analysis was done at Unit of Genetic Engineering and Biotechnology in Mansoura University according to the method of Wang et al. [16]. The sediment samples were dried at seventy degrees, sieved and digested for 2 hours using mixed acid (5 mL HCl, 3 mL HNO_3, 7 mL HF, 0.25 mL $HClO_4$) [17]. After the digestion, the concentrations of heavy metals (Pb, Cd, Cr, Ni, and Co) were estimated by Atomic Absorption Spectrophotometer (Buck Scientific Accusys 211, USA). Grain size and organic matters content (OM) in the sediment were estimated in accordance with the standard soil analysis assays [18].

Assessment of heavy metals contamination in sediments

The degree of pollution with each metal in Qarun Lake was determined using Indices such as contamination factor (Cf), geoaccumulation index (Igeo), ecological risk factor (Er), degree of contamination (Dc), and potential ecological risk index (PERI) were used for determination of pollution levels for each studied metal [19-23]. The equations used for estimating pollution indices and their classification are introduced in Tables 1 & 2.

Table 1. Different pollution indices equations used in this study.

Index	Formula	References
Contamination factor (C*f*)	$Cf = C_{sample} / C_{ref}$	[20]
Degree of contamination (D*c*)	$Dc = \sum_{i=1}^{n} Cfi$	[20,21]
Geoaccumulation index (I*geo*)	$Igeo = Log2\left(\frac{C_{sample}}{1.5Bn}\right)$	[19,22]
Ecological risk factor (E*r*)	$Er = Ti * Cf$	[20]
Integrated Potential ecological risk (IR)	$IR = \sum_{i=1}^{n} ER$	[23]

where: C_{sample}: metal concentration in soil analyzed sample; C_{ref} : (background) metal concentration in the reference environment; Bn: the geochemical background value in average shale of element *n*; 1.5: the background matrix correction due to terrigenous effects; Ti: the toxic-response factor for a given substance; Cf: the contamination factor.

Table 2. Classification of metals indices used in this study.

Index	Value	Soil quality
Contamination factor (CF)	CF < 1	Low **CF**
	1 ≤ CF ≤ 3	Moderate **CF**
	3 ≤ CF ≤ 6	Considerable **CF**
	6 ≤ CF	Very high **CF**
Degree of contamination (Dc)	DC < 8	Low DC
	8 ≤ Dc < 16	Moderate DC
	16 ≤ Dc < 32	Considerable DC
	Dc > 32	Very high DC
Geoaccumulation index (I*geo*)	I*geo* ≤ 0	Uncontaminated
	0 < I*geo* < 1	Uncontaminated to moderately contaminated
	1 < I*geo* < 2	Moderately to heavily contaminated
	2 < I*geo* < 3	Moderately to strongly contaminated
	3 < I*geo* < 4	Strongly contaminated
	4 < I*geo* < 5	Strongly to extremely contaminated
	I*geo* > 5	Extremely high contaminated

Ecological risk factor (Er)	$Er < 40$	Low **Er**
	$40 \leq Er < 80$	Moderate **Er**
	$80 \leq Er < 160$	Considerable **Er**
	$160 \leq Er < 320$	High **Er**
	$Er \geq 320$	Very high **Er**
Integrated Potential ecological risk (IR)	$IR < 150$	Low risk
	$150 \leq IR < 300$	Moderate
	$300 \leq IR < 600$	Considerable
	$IR \geq 600$	Very high

Geo-statistics

The geo-statistical analysis was conducted using the in ArcGIS (ver. 10.5) software to apply the ordinary Kriging method and the semivariogram among each pair of points against their separation spaces [24]. This semivariogram was conducted for prediction of the studied heavy metals in sediments of Qarun Lagoon.

Statistical analysis

Descriptive statistics were calculated for assessing the differences in heavy metal levels between the studied lake sites, and one-way ANOVA based on Duncan's test at the $p \leq 0.05$ probability levels was used for analyzing data, by the CoStat 6.3 program (CoHort Software, Monterey, CA, USA). Pearson moment correlation analysis was done for testing the linear dependence along heavy metals and sediment variables by SPSS software package ver.16 program. In addition, the data sediment analysis of the studied lake was subjected to principal component analysis (PCA) to build a matrix of correlation and to detect whether a significant difference presents between the treatments or not. Descriptive statistics and PCA were performed using PAST program (multivariate statistical package, ver. 1.72).

RESULTS AND DISCUSSION

Occurrence and abundance of heavy metals in sediment

Table 3 illustrates the descriptive statistics of the studied heavy metals concentrations (represented by dried weight) in the collected sediment samples from Qarun Lake. The concentration of Ni, Cd, Co, Cr, and Pb ranged in 14.44-45.40, 0.85-2.56, 5.18-16.34, 8.13-23.44 and 10.47-31.25 mg k g^{-1}, respectively. The average concentration ordered as Ni (27.36 mg k g^{-1}) > Pb (18.28 mg k g^{-1}) > Cr (15.31 mg k g^{-1}) > Co (11.16 mg k g^{-1}) > Cd (23.31 mg k g^{-1}). The concentration of heavy metals in the sediments of Lake Qarun is higher than that in the sediments of the Nile River (Damietta and Rosetta branches) which was considered as a background and a reference point and thus indicates significant contamination. In particular, Ni, Cr, and Pb have a higher level than the other studied heavy metals, which coincides with discharge and human activities around the Qarun Lake. The lower levels of the other heavy metals might be attributed to lower discharged amounts. The spatial distribution of heavy metals in the sediment of Qarun Lake could be demonstrated in Figure 2.

Table 3 also illustrates the levels of the heavy metals in other lakes of the Mediterranean coast, Egypt [25-27]. There is variability in the distribution of heavy metals along the northern lakes (Manzala, Burullus, and Idku Lakes). Manzala Lake expresses lower heavy metals concentration in sediment [25]. The Burullus Lake is located between Manzala and Idku Lakes and expresses higher heavy metals concentration in sediment (except for Cd) [26]. For the Idku Lake, the heavy metals levels in the sediment are higher than the studied lakes [27].

Spatial distribution of heavy metals

Figure 3 demonstrates the heavy metals levels at sites 1–12. The total heavy metals concentration increases at sites 1-3, then decreases at sites 4-9 but rises again at sites 10–12. Ni has the highest concentration at site 1 (45.40 mg k g^{-1}) followed by Site 5 (38.32 mg k g^{-1}). There is no significant difference in heavy metals concentrations in the north side (sites 4-9), but there is a significant difference within the south side (sites 1-3 and 10-12) (Figure 3b). The concentration of heavy metals is the highest on the south side, possibly according to the local pollution sources. Other parameters like grain size and organic matter (OM) content in sediments could also influence heavy metals levels. For example, more heavy metals adsorbed in sediment with elevated OM content [30]. The OM content on the south side is the highest among all sites.

Table 3. Descriptive statistics of heavy metal (mg K g^{-1}) in sediment samples from different sites (1-12) representing Qarun Lake and the concentration of the tested heavy metals in other lakes in Mediterranean coast, Egypt .

Statistic	Heavy metals (mg/Kg)					Reference
	Ni	Cd	Co	Cr	Pb	
Min	14.44	0.85	5.18	8.13	10.47	This study
Max	45.40	2.56	16.34	23.44	31.25	
Mean	27.36	1.64	11.16	15.31	18.28	
±SD	10.04	0.65	3.09	5.11	6.34	
Median	28.79	1.61	11.03	14.04	16.41	
CV %	36.70	39.74	27.68	33.38	34.69	
***p*-value**	0.03*	0.0044**	0.71ns	0.69ns	0.59ns	
Manzala Lake (n=31)	-	1.59±0.37	2.13±0.33	1.49±0.70	4.72±0.33	[25]
Burullus Lake (n=37)	-	0.69 ± 0.11	18.91 ± 4.27	53.91 ± 6.77	22.78 ± 7.66	[26]
Idku Lake (n=12)	14.11±2.54	14.74±1.69	23.75±3.22	22.07±2.88	30.92±4.67	[27]
Permissible limits worldwide						
EU (2002)	75	3	11.6	150	300	[28,29]
US EPA (1999)	19	0.01-41	9.1	54	19	
Average Shale	68	0.3	19	90	20	
Toxic factor	5	30	5	2	5	

SD: standard deviation; CV: coefficient of variation; EU: European Union Standard [28]; US EPA [29]. ***: significant at $p\leq0.001$, **: significant at $p\leq0.01$, *: significant at $p\leq0.05$, ^{ns}: non significance.

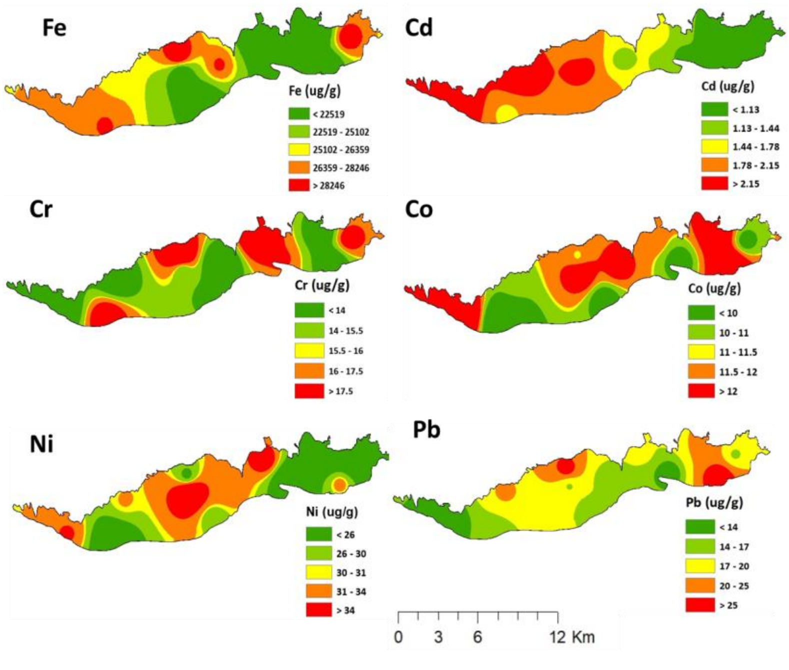

Figure 2. Spatial distribution of heavy metals in Qarun Lake

The marked distribution of various heavy metals may be corelated with specific environmental conditions and increased local human activities in specific locations more than the others [1, 31]. Nickel shows higher values other than the rest of the measured elements according to the observation from the obtained data of all the measured heavy metals, the high levels of nickel might because of agriculture drainage from the surrounding cultivated areas, the high levels of nickel might because of agriculture drainage from the surrounding cultivated areas (Table 3). Cadmium is a trace element used in the manufacturing of phosphatic fertilizers that considered being the main source of cadmium pollution besides atmospheric deposition [32]. Their highest concentrations are due to using pesticides and phosphate fertilizers used in agricultural activities [33]. The measured values of Cd in the studied lake were within EPA [29] and EU [28] permissible limits. Kesler and Simon [34] reported that the natural sources of cobalt in the environment are seawater, dust, or soil. The measured values of Co in the studied lake were lower than the limit of EU [28]. The source of Co in the studied lake might be attributed to industrial wastes that use the metal or its compounds, or from the wastes of phosphatic fertilizers [34,35]. The concentration of Cr in surface soil increases due to pollution from different sources of industrial wastes such as electroplating sludge, leather manufacturing wastes, Cr pigment, tannery wastes, and municipal sewage sludge [36]. Values of Cr in sediments of the lake are within EPA [29] and EU [28] permissible limits. Lead enters the aquatic ecosystem through precipitation of its dust, erosion and soil leaching, municipal and industrial waste discharge [28]. The mean values of Pb in sediments are within EPA [29] and EU [28] permissible limits (Table 3).

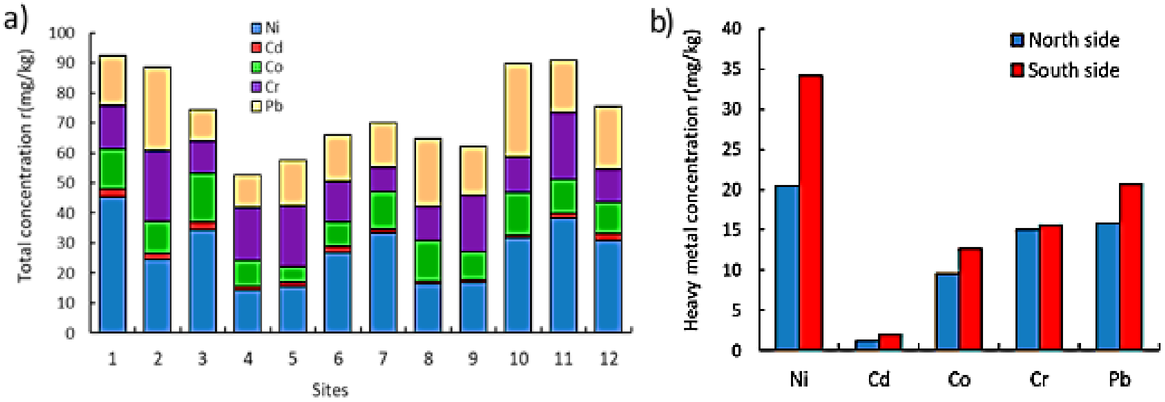

Figure 3. Spatial distribution of heavy metals in the sediment of the Qarun Lake **a)** different sites and **b)** south side, and the north side of the Qarun Lake

Assessment of heavy metals pollution

Contamination Factor (Cf) and degree of contamination (DC)

This index helps in monitoring of surface soil contamination over a while [20,37]. From the calculated C*f* values, low contaminations (C*f* < 1) were observed in observed in all sampling sites of Ni, Cr, and Pb (Figure 4a), and also the C*f* of Co showed low CF in sites 2, 5, 9, and 11 to moderate C*f* category in the rest of sites. The values of C*f* of Cd varied from moderate, considerable, and higher contamination factors. The sequence of C*f* for the mean concentration of heavy metals in the hydrosoils of Qarun Lake are as follows: Cd > Co > Pb > Ni > Cr. From that, cadmium expressed more abundance than other metals; whereas chromium expressed the lowest abundance. The dominance of Cd, Co, and Pb in the CF values is indication of anthropogenic involvement of heavy metals in Qarun Lake sediments. Moreover, Cd was the most enriched, especially in the sites close to the south. This can be due to the discharge from the agricultural runoff and domestic wastewater heavily contaminated with Cd [38, 39]. Moreover, the contamination degree (DC) illustrated those sites 4, 5, 7-

11 attained a low degree of contamination (DC < 8), while, there were a moderate level of contamination in sites 1-3, 6, and 12 (8 ≤ Dc < 16). According to Liu et al. [40], the obtained results illustrted severe anthropogenic pollution of the studied lake which needs to be monitored. Contaminants are translocated from agricultural land, sewage, and tributaries then deposited into urban rivers and lakes.

Geo-accumulation index (Igeo)

The Geoaccumulation Index (I*geo*) is an indicator used for assessing the presence of heavy metals accumulation in the sediments. The I*geo* was determined for the reference element which is an element particularly stable in the soil [41]. Similarly, the geo-accumulation index values expressed a positive result for the sites near the drains outlets on the south side of the lake (Figure 4b). The negative values of Ni, Co, Cr, and Pb based on the classification of Muller [19] showed that there is no pollution with these metals in the Lake. For Cd, the values of Igeo expressed moderate pollution level, with descending order Cd, Pb, Ni, Cr and Co, respectively.

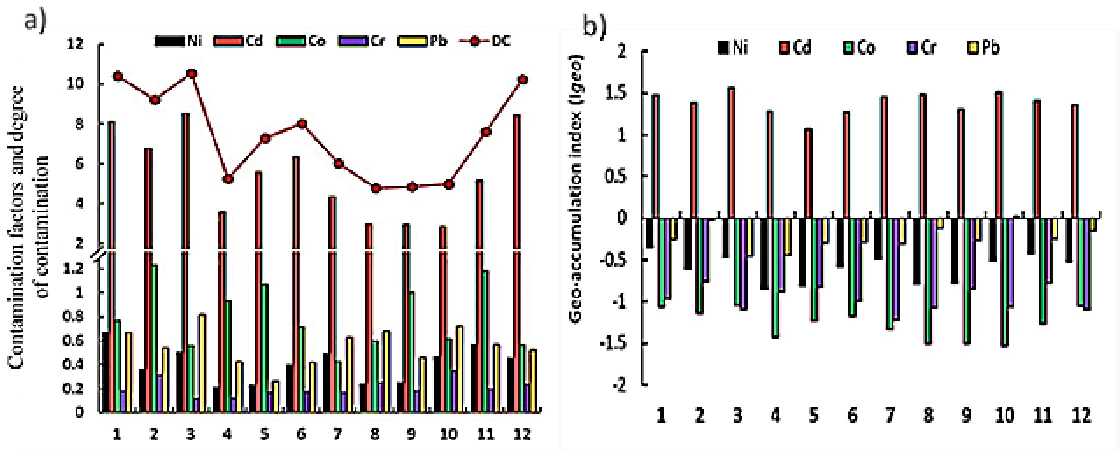

Figure 4. a) The contamination factors (CF) and degree of contamination (DC), and **b**) geo-accumulation index (I*geo*) of heavy metals in the sediment samples of Qarun Lake.

Ecological risk assessment

Environmental risk assessments (ERA) are performed to assess the potential for adverse ecological impacts from exposure to physical or chemical stresses. These stressors are defined as any biological, physical, or chemical agent that causes negative reactions in the environment [42, 39]. In this study, the ecological risk assessment was estimated using 2 risk indices viz. potential ecological risk index (RI). The outputs of Er and IR evaluation are illustrated in Figure 5. The Er of heavy metals in sediments of lake could be arranged descendingly as Ni, Pb, Co, Cd and Cr.

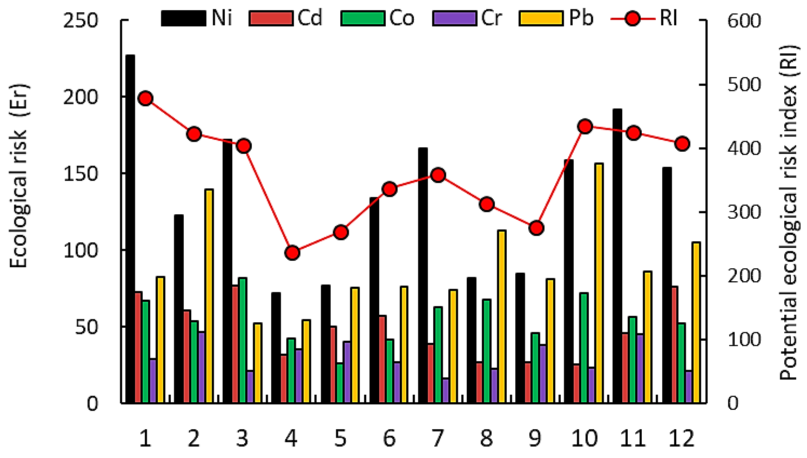

Figure 5. Pollution indices (Er and RI) in the sediment samples of Qarun Lake.

A low mean value of Er index of Cd and Cr in the analyzed (selected) sites were 16.26-46.88 and 26-77, respectively (i.e., ranged from moderate (40 < Er < 80) to considerable (80 < Er < 160) to higher (160 < Er < 320) ecological risk). The mean value of Er index of Co varied from 25.90 to 81.70. Meanwhile, a moderate mean value of Er index of Pb and Ni was 52.35-156.25 and 72.20-227 in the lake, respectively (Figure 5). The results of the integrated potential ecological risk index values reported in Qarun lake range from moderate (150 ≤ RI < 300) to considerable (300 ≤ IR < 600) ecological risk. Figure 5, shows that most of the highest-integrated potential ecological risk area was on the south side of the lake, which is exposing to massive amounts of drainage water containing organic and inorganic pollutants. The degree of pollution and ecological vulnerability of Qarun Lake increased in front of the El-Bats and El-Wadi drains (the south side), according to El-Zeiny et al. [43].

Risk index could be distinctive for the sensitivity of the local environment to the toxic metals and express ecological risk resulted from the overall contamination [42]. According to El-Amier et al. [27], all metals in Idku Lake had low potential ecological risk (< 40), except for Cd which showed very high ecological risk (> 320) and the risk index values recorded very high ecological risk (> 600).

Influences of different environmental parameters on heavy metals levels

By applying the Pearson correlations between the five selected heavy metals and the environmental variables (sand, silt, clay, and organic matter (OM)), (Table 4). Overall, the heavy metals concentrations are negatively correlated with the sand, while positively correlated with the silt, clay, and OM. Xiao et al. [45] illustrated that the heavy metals levels increase with decreasing the sediment pore size. The results showed that Ni is well correlated with OM, Cd, Co, and Cr (r = 0.611, 0.641, 0.587, -0.667, respectively). Furthermore, there is a correlation between Co and each of Cr and OM (r = -0.594, 0.638, respectively). There are significant correlations between Cr and each of silt and clay (r=0.568, 0.665, respectively) as shown in Table 4. Organic matter makes strong complexes with heavy metals [30]. Moreover, the Cd, Co, and Ni are correlated with sites 3, 4, and 6. While among the south sites 1, 2, 10, and 12 are correlated with Cr and Pb.

The PCA analysis was conducted for investigating the influence of environmental variables on heavy metals distributions, as demonstrated in Figure 6. The lengths of the environmental variables arrows indicate the degree of relevance, and that there are greater correlations between heavy metals concentrations, fine sediments and OM, this could also be concluded from Table 4. According to Ciazela and Siepak [45], the metals concentrations were highly affected by the soils granulometric composition.

Table 4. Correlation analysis between the heavy metals concentration and environmental variables in Qarun Lake. The significant values are in the bold letters. *P < 0.05, **P < 0.01.

	Sand	**Silt**	**Clay**	**OM**	**Ni**	**Cd**	**Co**	**Cr**
Ni	-0.159	0.110	0.236	**0.611***	1			
Cd	-0.329	0.315	0.342	0.213	**0.641***	1		
Co	-0.083	0.142	0.018	**0.638***	**0.587***	0.135	1	
Cr	-0.207	**0.568***	**0.665***	0.049	**-0.667***	**-0.575***	**-0.594***	1
Pb	-0.192	0.112	0.254	0.074	0.042	-0.211	0.222	0.06

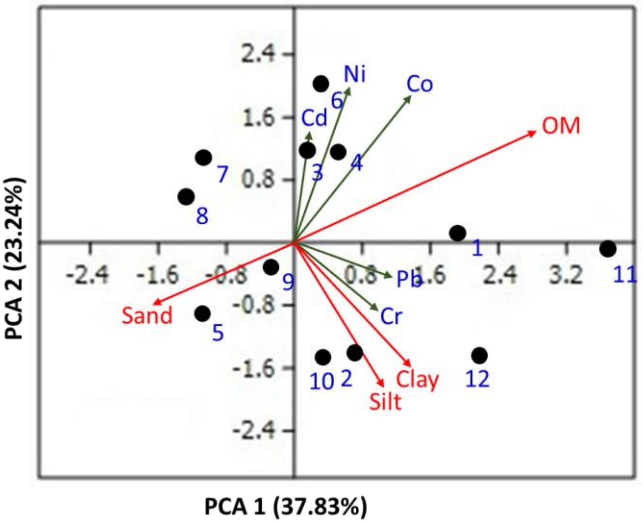

Figure 6. Principal component analysis (PCA) of heavy metals and environment variables.

CONCLUSIONS

The obtained data regarding the different pollution indices (Cf, Igeo, Er, Dc, and PERI) of the sediment heavy metals in Qarun Lake showed that heavy metal concentration was higher on the south side than on the north side. The average concentration ranked as Ni > Pb > Cr > Co > Cd. Cd, Co and Pb were found to be in the range of EU (2002) and the US EPA (1999) limits, while Co and Ni within the EU (2002). The sequence of Cf for the mean concentration of heavy metals in the hydrosoils of Qarun Lake are as follows: Cd > Co > Pb > Ni > Cr. As a result, cadmium is more abundant than other metals, while chromium seems to be the least abundant. While, the ecological risk index (Er) of heavy metals in sediments of lake could be ordered as: Ni > Pb > Co > Cd > Cr. In contrast, the biological risk index (Er) of heavy metals in lake sediments is as follows: Ni > Pb > Co > Cd > Cr. Furthermore, the south side of the lake, which is exposed to large volumes of runoff water containing organic matter, posed the highest-integrated possible ecological danger.

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Conflict of interests

The authors declared no conflict of interest

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