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Chemical fractions and ecological risk of metals in sediments of the Bitter Lakes, Egypt.

Naglaa F. Soliman[1,2] **, Eman M. Elkady**[3] **and Alaa M. Younis**[4]
[1]Department of Environmental Studies, Institute of Graduate Studies & Research, Alexandria University, Egypt.
[2]Technology Management Department, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, Egypt
[3]Marine Chemistry Lab, National Institute of Oceanography & Fisheries, Cairo, Egypt
[4]Department of Aquatic Environment, Faculty of Fish Resources, Suez University, Suez, Egypt.

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ABSTRACT

Total levels and fractions of metals (Cd, Cr, Fe, Mn, Ni and Pb) in sediments of the Bitter Lakes were attained and several indices and guidelines were used to evaluate pollution and potential risk. Metal contents revealed a clear spatial distribution in the sediments mainly for Cr, Mn, and Ni, which may be caused by human inputs of metals, and predominant physicochemical conditions and complex reactions proceeding in the sediments. Sequential extractions showed that all metals were mostly composed of residual and Fe/Mn-oxide bound fractions.

All potential risk indices depended on the bioavailable fractions contents such as risk assessment code (RAC), individual contamination factor (ICF), and modified potential ecological risk factor (E_r^i-A) proposed that Cd had the lowermost ecological concern, demonstrating slight reactivity in the lake ecosystem, and consequently presented low risk. Whereas risk assessment indices dependent on the total metal contents represented by threshold and probable effect level (TEL-PEL approach) and potential ecological risk factor (E_r^i) designated that most Cd was in a highly individual potential ecological risk. Numerous indices that estimated from the measurements of total and chemical fractions concentrations should be conducted to make the risk assessment procedures precise and consistent in the investigation of deposited metals.

INTRODUCTION

Pollution of aquatic ecosystems by metals, particularly in sediments, is one of the most stimulating contamination problems as a result of the toxicity, abundance, considerable non-degradability, and consequent bioaccumulation of these contaminants **(Barlas *et al.*, 2005; Shreadah et al., 2006; Fu *et al.*, 2014; Amin *et al.*, 2018; Younis, *et al.*, 2019; Saleh *et al.*, 2019; Younis, *et al.*, 2020; Younis, 2020).** Below 0.1% of the metals are essentially dissolved in the water, and above than 99.9% are deposited in sediments **(Pradit *et al.*, 2013)**. Lake sediments serve as a main depository of metals and considered a cause of pollution for aquatic organisms and the water column. Sediments are important media for metal valuations as it deliberated as an intermediate and/or long-term integrator of metal contribution **(Dar *et al.*, 2018).** Sediments may either leach metals to the overlying water or act as an origin of metals for ecotoxicity and biological magnification in aquatic organisms and lead to decrease in desired biodiversity **(Zhang *et al.*, 2017)**. Soil erosion, atmospheric fallouts, geological weathering and human intrusions comprising fertilizer leakage, untreated domestic wastewaters, industrial effluents, and urbanization are influences that permit metals to come into the lakes **(Kankılıç *et al.*, 2013).** Without human activities, metals in sediments are mostly bound to silicates and primary mineral deposits and consequently have restricted bioavailability. On the other hand, metals imported by anthropogenic contributions are more mobile. They are bound to other sediment fractions, for instance, carbonates, oxides, hydroxides and sulfides **(Passos *et al.*, 2010; Younis, 2018).**

Many investigators demonstrated that the total content of metals don't control its mobility and toxicity in sediments **(USEPA 2005)**. Metal fractionation in sediments is an essential technique. It offers supplementary data correlated to prospective mobilization, bioavailability and geochemical forms of a specific metal **(Yang *et al.*, 2009; Soliman *et al.*, 2019).** Recently, sequential extraction techniques, consuming several extracting chemicals and operational conditions, have been conducted to acquire data related to metals bonding fractions and origins in sediments **(Nasr *et al.*, 2015; Sakan *et al.*, 2016; Rosado *et al.*, 2016; Soliman *et al.*, 2019)**. Amongst metal forms, exchangeable and carbonate binding forms are more mobile, and define both the bio-accumulation and bio-magnification in the aquatic food chain **(Sundaray *et al.*, 2011; Amin *et al.*, 2018; Younis *et al.*, 2018).** Hence, a comprehensive evaluation of manmade metal inputs to the ecosystem would therefore reflect both the total and bioavailable metal forms. The Bitter Lakes is a part of the Suez Canal. It is also considered as a valued fishing area. It has a wonderful beach for tourism. Furthermore, it characterized by multiple resource ecosystems that are endangered by anthropogenic influences such as tourist villages, fish landing sites, agricultural lands, and electric power station. These intrusions disturb the water quality of the lakes **(Madkour, 1992).**

To our knowledge, no information is obtainable on the association among the diverse geochemical forms of metals in sediments of the Bitter Lakes. Hence, evaluating the pollution and environmental risks of metals in sediment by several indices that are originated from the different metal evaluation approaches and spatial analysis tools is significant. The evaluation may assist in describing the pollution origins in sediments and offer a mean for efficiently preserving the lake ecosystem.

Consequently, the aims of this work were (1) to evaluate metal dynamics and their mobilization in diverse chemical forms of sediment; (2) to recognize the bioavailability and ecological risk of these metals in the sediment; (3) classify the main sources of metals by correlation analysis. The outcomes of this work may be applied by administrators to assess the sediment contamination and take effective policies for pollution abatement.

MATERIALS AND METHODS

2.1. Study area for the Great Bitter Lake

The Bitter Lakes (30°20′ N, 32°23′ E) are the largest water bodies along the Suez Canal **(Hamed *et al.,* 2012)** (Fig. 1). They constitutes about 24% of the canal with a total length of 39 km and depth between 6 m and 28 m with a total surface area of about 250 km^2 and 85% of the water of the Suez Canal System. The lake is extensively used in fishing, tourism and aquaculture besides other recreational activities. It suffers from various kinds of human activities such as; the agricultural runoffs from adjacent cultivated lands, domestic wastewater from the nearby human settlements, in addition to the industrial and thermal pollution **(El-Serehy *et al.,* 2018).**

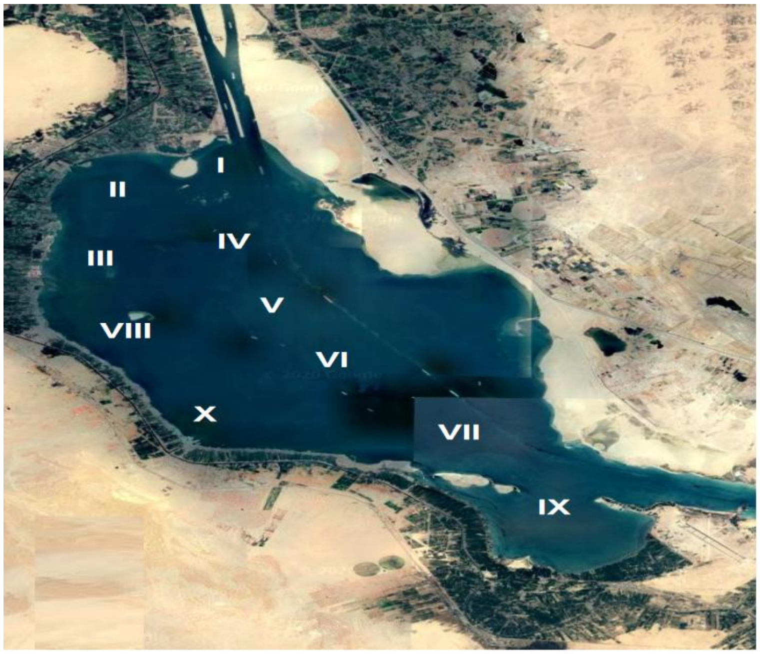

Fig.1. Study area for the Great Bitter Lake

2.2. Sediment collection and preparation

Sediments samples (0 - 10 cm) from 10 different sampling sites in the Great Bitter Lake were collected using a Peterson grab sampler in July 2019. Sampling sites were carefully chosen based on the closeness and remoteness of human intrusions (some sites nearby the electric power plant, agricultural and domestic wastewater, along with discharges from ships and fishing boats and some others far from them). At each sampling site, three subsamples were taken and then homogenized together to get a composite sample. Sediment samples were then packed into polyethylene bags and stored at - 20 °C until further investigation.

2.3. Physicochemical Characterization

Total (TP), organic (OP) and inorganic (IP) phosphorus concentrations were carried out according to Aspila (1976). Sediment particle size has been analyzed using a standard sieving technique **(Folk, 1974).** Total organic carbon (TOC) content was evaluated by wet oxidation method **(Loring and Rantala, 1992).** Carbonate (TCO_3) content was measured on the basis of

Black (1965). All data pertaining to the sediments in this work were described on a dry weight basis.

2.4. Sediment digestion, metal extraction, and analysis

All reagents used were of analytical grade, while water was double distilled. Teflon and polypropylene containers were cleaned, soaked in 5% nitric acid for 24 h, and then washed with double distilled water. The analysis of total metals in the sediments was accomplished relative to Oregioni and Aston **(1984)**. Metal fractionation in the sediment was performed as corresponding to Tessier sequential extraction protocol **(Tessier *et al.*, 1979)** into five fractions: F1-exchangeable: those metals which are deliberated to be weakly bound and most easily bioavailable **(Samhan *et al.* 2014; Martin *et al.* 2015)**; F2-bound to carbonates: these metals are inadequately bound to the sediment. It may be leached to the pore water in acidic circumstances (pH < 5) **(Zakir and Shikazono 2011)**; F3-bound to Fe and Mn oxides: these oxides are scavengers for metals and thermodynamically unstable under anoxic circumstances **(Malsiu *et al.*, 2020)**; F4-bound to organic matter: This fraction of metals may present in the sediment for extended times, and may be leached during decomposition of organic matter **(Peng *et al.* 2009)**; and F5-residual: are confined in primary and secondary minerals within their crystalline lattice **(Bastami *et al.*, 2016)**.

Overall, the mobilization and metals bioavailability in soil and sediment decline with the trend of the extraction sequence (Exchangeable > carbonates > Fe/Mn oxides > organic > residual) **(Tessier *et al.*, 1979)**. The exchangeable, bound to carbonates and bound to Fe/Mn oxides are more mobile and bioavailable than the bound to organic matter and residual fractions **(Tessier, 1979)**. Carbonates and Fe and Mn oxides, as well as exchangeable fractions, may subsidize to remobilization of heavy metals, accordingly causing ecological risk through ion exchange and dissolution **(Lee *et al.*, 2017).**

The contents of metals in the extracted fractions were measured by atomic absorption spectrophotometer (AA-6800 Shimadzu). Quality control was confirmed through duplicates, method blanks, and standard reference material (IAEA-405). Recovery rates were in the range of 92%–97% for all metals and the relative standard deviation was lower than 10%.

2.5. Evaluation of mobility, ecological risk and source identification of metals

Fractionation of selected metals into different chemical forms has been performed to determine in which forms these metals are chemically chelated in the sediments from the Great Bitter Lake, in addition to distinguish between resistant metals (natural background) and non-resistant ones (anthropogenic sources of pollution).

The integrated ecological risk of the investigated metals was also appraised with the results of the total metal contents through the potential ecological risk index (RI) and the results of sequential extraction through Global contamination factor (GCF), modified risk assessment code (mRAC), modified potential ecological risk index (mRI), and the mean quotients corresponding to the sediment quality guidelines (SQGs).

The data analysis tool of Microsoft Excel 2016 was utilized for data analysis: the calculation of the average, coefficient of variance (CV) and relative standard deviation (SD). Pearson's correlation analysis was done to examine the correlation amongst the sediment factors analyzed using Minitab 17 Statistical software. Analysis of the matrix offers indications about carrier substances and the geochemical relationship of metals in the sediments **(Forstner and Witman, 1983).**

RESULTS AND DISCUSSION

3.1. Physicochemical characteristics of sediments

The physicochemical properties of the sediments are presented in Table 1. Sand fraction is shown to be the dominant form (14.80 to 96.66%; average: 59.58%) followed by silt (1.50 to 83.20%; average: 32.23%) and clay (0.70 to 20.40%; average: 8.19%). Generally, the sediments of the Great Bitter lake are mostly consisted of sand and silt and this might be owing to continual drilling operations to deepen and expand the Suez Canal in addition to increase the filling of beaches for tourism activities **(Belal and Dar, 2020).** Organic carbon content of sediments in the Great Bitter Lake ranges from 0.28 to 2.96% with an average value of 1.46%. The carbonate content varies from 6.80% to 7.30% with an average value of 7.04%. In general, carbonate contents in the Great Bitter lake are considerably low, demonstrating the influx of terrigenous materials **(Soliman *et al.*, 2019).** According to **Maxwell (1968)** classification, all sediments are of elevated terrigenous materials with a carbonate content less than 20%.

The results of total, inorganic, and organic phosphorus content are displayed in Table 1. Total phosphorus (TP) contents are in generally low, alternating from 140 to 703 µg/g. In relation to the Canadian SQGs **(Mudroch and Azcue, 1995),** TP contents at 30% of the sampling sites (sites: 2, 3, and 10) in the Great Bitter Lake exceed the lower sediment quality guideline of 550µg/g, signifying that there is a great level of toxic effects on sediment dwelling organisms from TP at these sites. Sites 2 and 3 are situated nearby Abu Sultan Power Station, this area are subjected to huge quantities of industrial contaminants from the power plant, agricultural and domestic wastewater, and discharges from ships and fishing boats **(Abd El-Azim *et al.*, 2017).** While, station 10 is nearby to the outlet of Malaria Drain, which is one of the greatest drains from Ismailia Town. It also receives agricultural and industrial effluents from settlements nearby to the lakes **(El-Bassat, 2008).**

It can be seen in Table 1 that inorganic phosphorus (IP) is the abundant form (about 70% of the TP). Inorganic phosphorus level ranges from 123 to 504 µg/g. The level range of organic phosphorus is 17 to 389 µg/g (about 30% of the TP). This is a substantial character discriminating sediments from soils, where organic phosphorus prevails **(Gunduz *et al.*, 2011).**

Table 1: Physicochemical characteristics of sediments in the Great Bitter Lake

Sites	TOC (%)	TCO_3 (%)	TP (µg/g)	IP (µg/g)	OP (µg/g)	Grain size analysis		
						Sand (%)	Silt (%)	Clay (%)
1	0.3	7.01	140	123	17	96.66	1.50	1.84
2	2.96	7	701	504	197	20.10	59.60	20.30
3	2.78	7.02	703	314	389	20.80	58.80	20.40
4	1.01	6.9	420	244	176	74.60	12.70	12.70
5	0.29	7.1	210	170	40	93.20	2.00	4.80
6	0.28	7.3	390	290	100	60.00	28.40	11.60
7	0.84	7.1	300	275	25	90.50	8.50	1.00
8	2.82	7.02	485	375	110	40.70	52.70	6.60
9	0.35	7.15	340	240	100	84.40	14.90	0.70
10	2.95	6.8	610	490	120	14.80	83.20	2.00
Average	1.46	7.04	429.9	302.5	127.4	59.58	32.23	8.19
Min	0.28	6.80	140.0	123.0	17.0	14.80	1.50	0.70
Max	2.96	7.30	703.0	504.0	389.0	96.66	83.20	20.40
SD	1.25	0.14	195.1	124.3	109.4	32.88	29.04	7.66

3.2. Distribution and sources of metals in the sediment

The spatial distribution of total metal contents in sediments of the Great Bitter Lake are illustrated in Fig. 2. Range contents of Cd, Cr, Fe, Mn, Ni, and are 0.75-2.24 µg/g, 3.3-35.40 µg/g, 2800-3900 µg/g, 123.56-495.28 µg/g, 8.85-32.55 µg/g, and 6.77-29.87 µg/g, respectively (Table 2). Total metal contents in sediments of the Bitter Lake follow the trend: Fe>Mn>Pb>Ni>Cr>Cd. The coefficient of variation (CV) for Cr in the sediments is as high as 55.03%, followed by Mn (CV: 44.99%) and Ni (CV: 42.01%) (Table 2).

This designates the comparatively large differences in total Cr, Mn, and Ni concentrations in sediments, which may possibly due to human inputs of metals **(Huang *et al.*, 2019),** and prevalent physicochemical circumstances and complex reactions such as adsorption, flocculation and redox condition happening in the sediments **(Sekhara et al., 2003).** While the lowermost metal variation is observed for Fe (CV: 12.74%), demonstrating a homogeneous concentration of this metal in the designated sites **(Bastami *et al.*, 2016).** A similar result was reported by **Soliman *et al.* (2019),** where the spatial distribution of Fe in El Temsah Lake sediments (the Suez Canal) was quite uniform across the sampling sites and this was consistent with its small CV.

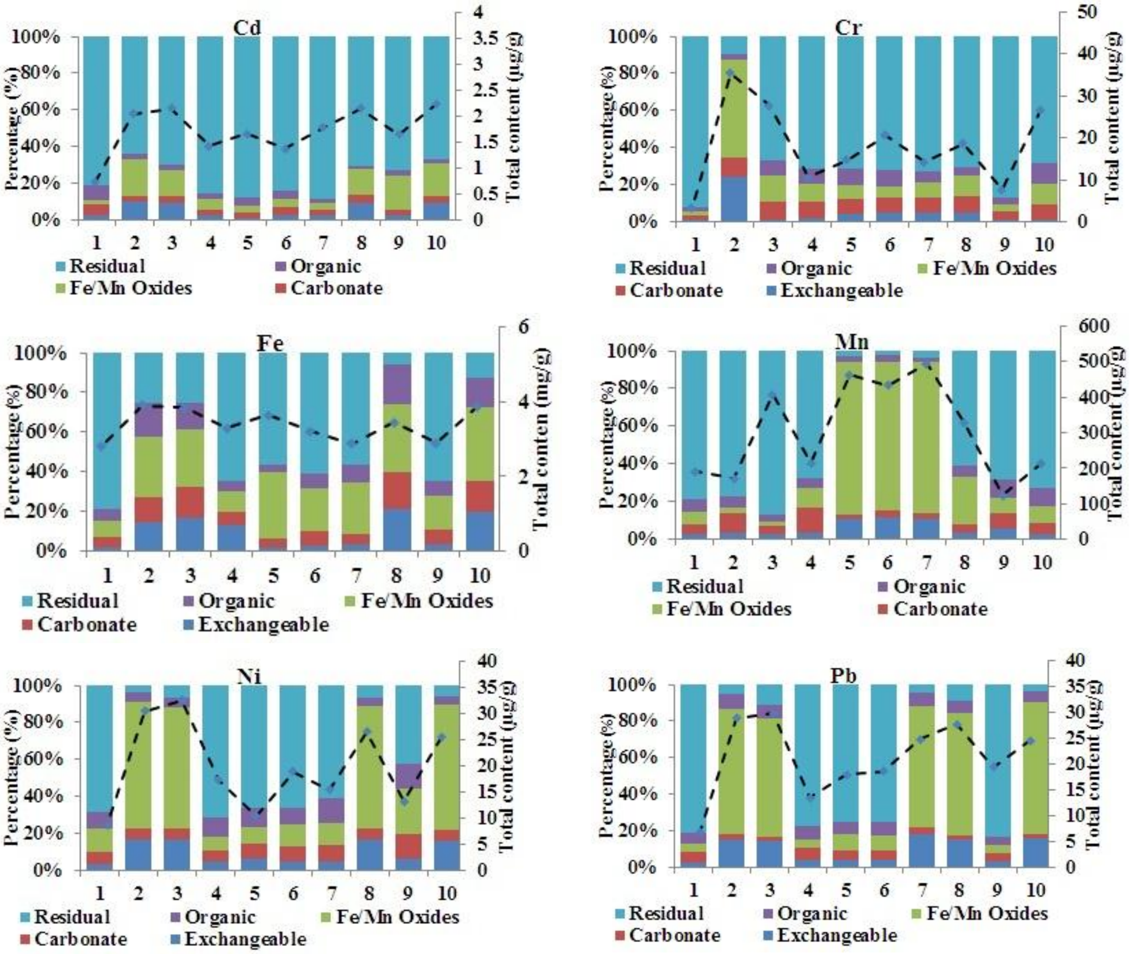

Fig. 2. Spatial variations of metals in total contents (µg/g) and their distribution in different fractions in sediments from the Bitter Lakes

Table 2. Descriptive statistics of total metal contents in sediments from the Great Bitter Lake

	Cd (µg/g)	Cr (µg/g)	Fe (mg/g)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)
Min	0.75	3.30	2800	123.56	8.85	6.77
Max	2.24	35.40	3900	495.28	32.55	29.87
SD	0.46	9.90	430.91	136.84	8.38	7.37
Average	1.72	17.99	3380	304.14	19.95	21.24
CV	26.67	55.03	12.74	44.99	42.01	34.69
Average Shale	0.3	90	47000	850	68	20
TEL	0.68	52.3	NA	NA	15.9	30.2
PEL	4.21	160	NA	NA	42.8	112

NA; Not available

Amongst the studied metals, Fe and Mn are shown to be the most abundant metals, followed by Pb, Ni and Cr while Cd contents are the lowermost. The maximum contents of Fe and Cr are found at site 2, while the maximum contents of Ni and Pb are found at site 3. This elevation in metal contents is owing to the release of water from the electric power station (Abu Sultan), where the cooling device discharges around 101752 m^3/h **(El-Bassat, 2008).**

Moreover, the maximum levels of Mn and Cd observed at site 7 and 10, respectively. Site 7 is situated nearby Fanara, that is characterized by tourist villages, agricultural areas, and Fanara fish landing site. Also, elevated levels of Cd, could be owing to agricultural and industrial activities nearby the lakes **(El-Bassat, 2008).**

Overall, the maximum contents of toxic metals are observed at that sites which are enriched with silt/clay. These results agree with **Belal and Dar (2020)** who indicated the role of fine-grained fractions (silt and clay) in elevating the metal contents, since they possess greater surface area than the coarse fractions (sand). Moreover, the phases of crushing metals including Fe/Mn hydrate, organic carbon, clay minerals are greater in fine-grained fractions than in coarse fractions **(Padmalal *et al.*, 1997).**

On the other hand, site 1 is offshore and situated in the Defersoir zone and consequently is away from the causes of contamination. Consequently, the lowermost contents of Cd, Cr, Fe, Ni and Pb (0.75, 3.30, 2800, 8.85 and 6.77 µg/g, respectively) are registered in the sediments.

The geochemical background is significant in discriminating whether a metal found in the environment appears naturally or, on the contrary, has been affected by man-made activities **(Hernández-Crespo and Martín, 2015).** Baseline values of metals in lake sediment is a lake-specific owing to dissimilarities in bedrock, soil kind and sediment texture. In this work, the average shale background concentrations **(Turekian and Wedepohl 1961),** was considered as the natural baselines utilized for pollution and ecological risk assessment **(Soliman *et al.*, 2018).** The contents of Cr, Fe, Mn, Ni, and Pb in the sediments of the Great Bitter Lake are all lesser than the background values in the average shale **(Turekian and Wedepohl 1961),** while the contamination level of Cd is nearly 5 times greater in the sediment than in the average shale, signifying that added anthropogenic Cd may have been introduced into the lake through the recent economic development.

3.3. Metal fractionation

It is recognized that the role of aquatic sediments as a depository for metal contamination can’t be totally evaluated by determining the total metal content. Determination of the total metal content gives only a general evaluation of the prospective ecological impact **(Gupta and Sinha, 2007).** So, it is recommended to obtain data on the expected bioavailability and mobility of metals to aquatic organisms under diverse environmental circumstances. Taking into account that the probable mobilization, bioavailability, and toxicity of metals in sediment are not only linked with their total levels, but also mostly rely on their geochemical fractionation **(Fuentes et al., 2004),** significant interests exist in metal fractionation **(Davidson *et al.* 1994).** Accordingly, for discovering the mechanisms controlling metal fractionation with diverse depository phases and mobilization in the Bitter Lakes sediments, sequential extraction procedure was performed to acquire data on the processes and strength of sediment-metal binding state on redox sensitive elements (Fe and Mn) and heavy metals Cd, Cr, and Pb. Among metal forms, exchangeable and carbonates bound fractions are considered to be bioavailable, and define both the biotoxicity and biological magnification in the aquatic food chain **(Sundaray *et al.*, 2011).**

The fractions of metal contents that were measured in each stage of the sequential extraction process are illustrated in Fig. 2. The speciation pattern and fractionation behavior of metals in sediments of the Great Bitter Lake are: Residual > Fe/Mn oxides > carbonates > organic > exchangeable for Cd, residual > Fe/Mn oxides > carbonates > organic > exchangeable for Cr, residual > Fe/Mn oxides > organic > carbonates > exchangeable for Fe, residual > Fe/Mn oxides > carbonates > organic > exchangeable for Mn, residual > Fe/Mn oxides > exchangeable > organic > carbonates for Ni, Residual> Fe/Mn oxides> Exchangeable>Organic>carbonate for Pb.

The fractionation behavior suggested that all the considered metals are dominated by residual phases. The extractability percent order of metals in the residual fraction follow the rank Cd>Cr>Mn>Fe>Pb>Ni. The higher proportions of total residual fractions with respect to non-residual fractions of Cd (77.34%), Cr (68.33%), and Mn (52.3%) designate that maximum contents of these metals are extremely bound to the sediments **(Benson *et al.*, 2017).** It is also, recommended that the origins of these metals in sediments may be derived principally from geological processes under natural field conditions **(Naji and Sohrabi, 2015).** While, lower than 50% contribution of other metals (45.2%, 42.5% and 39.9% on average for Fe, Pb and Ni, respectively) in the residual phase expose that natural origin is not the principle origin of these metals the Bitter Lakes sediments.

Amongst the non-residual fractions, the Fe-Mn oxyhydroxide is the main binding form for almost all metals in the sediments (36.9%, 34.5%, 30.6 and 24.9% on average for Pb, Ni, Mn and Fe, respectively). This might be attributable to the adsorption, flocculation, and coprecipitation of metals with the colloids of Fe and Mn oxyhydroxide **(Passos *et al.*, 2010).** The exchangeable fraction accounted for 9.6%, 9.6%, and 9.4% of total Pb, Fe, and Ni levels in the sediment, respectively (Fig. 2). The observed proportions of exchangeable Pb, Fe, and Ni expose that these metals may have a toxic effect to benthic organisms in the lake and local inhabitants. This form of metals may be leached readily and available for marine organisms.

Moreover, Fe and Ni in the organic bound fraction was more abundant (average 10.4% and 8.6%, respectively) compared to other metals (3.5%, 6.6%, 5.6%, and 6.9% for Cd, Cr, Mn and Pb, respectively). The association of Fe, and Ni with organic bound form has been reported in many investigations **(Passos *et al.*, 2010; Samhan *et al.*, 2014; Soliman *et al.*, 2019).**

Also, it can be seen that (9.9%, 7.6%, 7.6%, and 6% of Fe, Cr, Ni, and Mn, respectively, are combined with carbonates bound fraction and a slight portion of Cd and Pb (3.7 and 4.1%, respectively) are observed in this fraction. Proportions of these metals in the carbonate form would entail that metals may be easily available succeeding a slight decreasing of pH **(Zakir and Shikazono, 2011).**

3.4. Evaluation of metal dynamics and mobility in geochemical fractions

Figure 3 matches non-resistant (Exchangeable, carbonates, Fe/Mn oxides and organic) fractions with resistant (residual) fraction in the sediments of the Great Bitter Lake.

The mobilization order of metals based on the sum of the quantities of non-resistant fractions for all the sediment samples are in the sequence: Ni (60.15%) > Pb (57.49%) > Fe (54.83%) > Mn (47.74%) > Cr (31.67%) > Cd (22.66%). It was distinguished that Ni, Pb, Fe and Mn had >40% exist in possibly mobile fractions and consequently, may be the more easily mobilized and bioavailable metals in the sediments of the Bitter Lakes. While, Cd and Cr had comparatively lesser amounts exist in the mobile fractions. Heavy metals in the non-resistant fractions are most bioavailable than in resistant fraction **(Larner *et al.*, 2006)**. High concentrations in the bioavailable fractions may produce severe ecological risks. Consistent with **Brady *et al.* (2014),** fluctuations in environmental conditions frequently lead these metals to become readily bioavailable **(Delshab *et al.*, 2016)** and may have opposing toxic threats on benthic organisms in the lake.

Relatively great probable bioavailability of Cr is observed at site 2; Fe at sites 2, 3, 8, and 10; Mn at sites 5, 6, and 7; Ni at sites 2, 3, 8, 9, and 10; Pb at sites 2, 3, 7, 8, and 10 (Fig. 4). A remarkable trend is that the nonresistant fractions are considerably greater in sediments from the same sampling sites with elevated total concentration of metals. The maximum contents of Cr, Fe, Mn, Ni, and Pb in bioavailable forms may be imported by human intrusions, such as agricultural runoffs from the cultivated lands, municipal effluents along with the thermal and industrial contamination **(El-Serehy *et al.*, 2018).** This also inferred that human intrusions not only affect the total metal levels of these metals but also their fractionation profiles in the lake sediments.

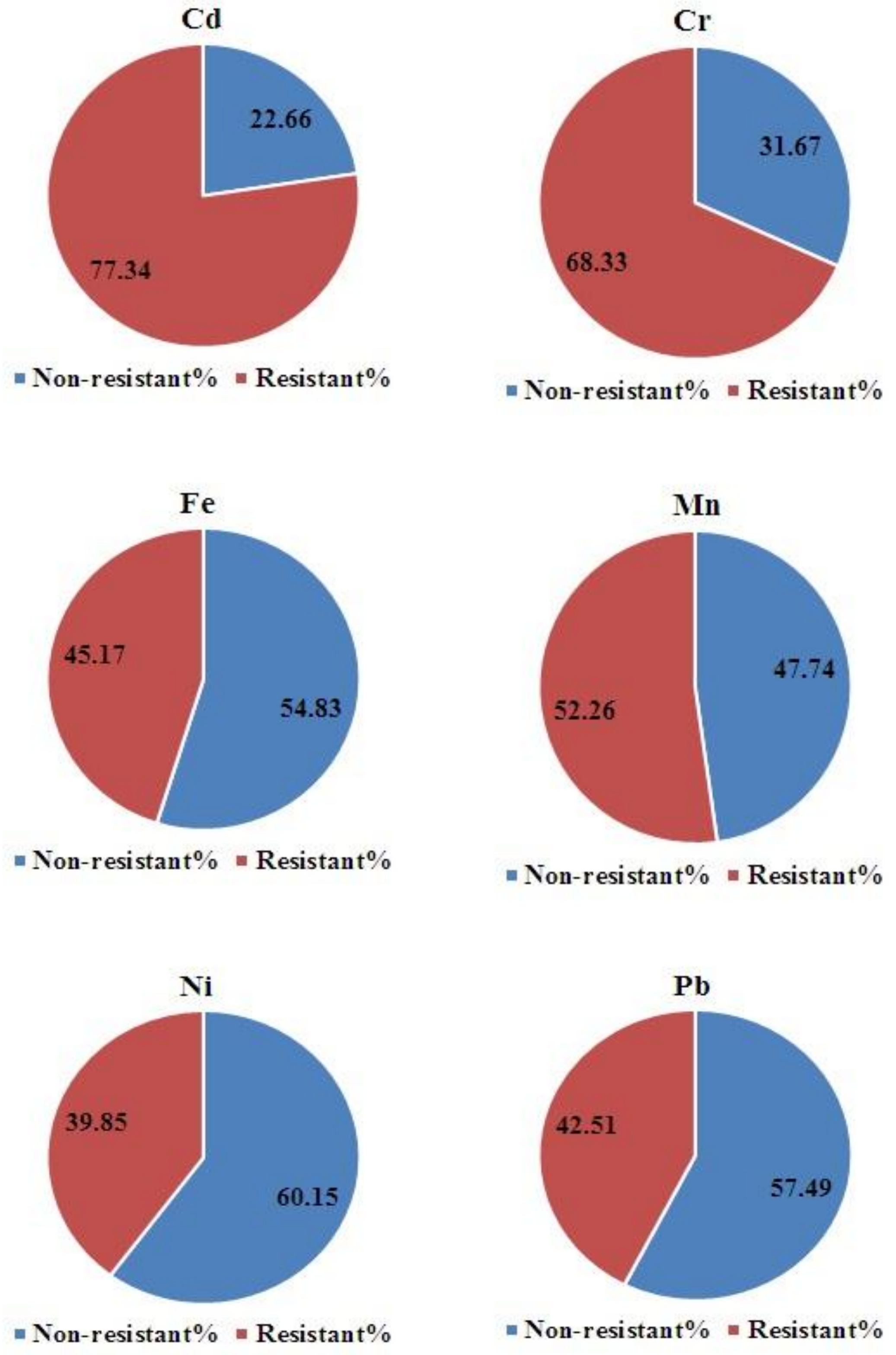

Fig. 3. Percentages (%) of resistant and nonresistant fractions of metals from the Great Bitter Lake.

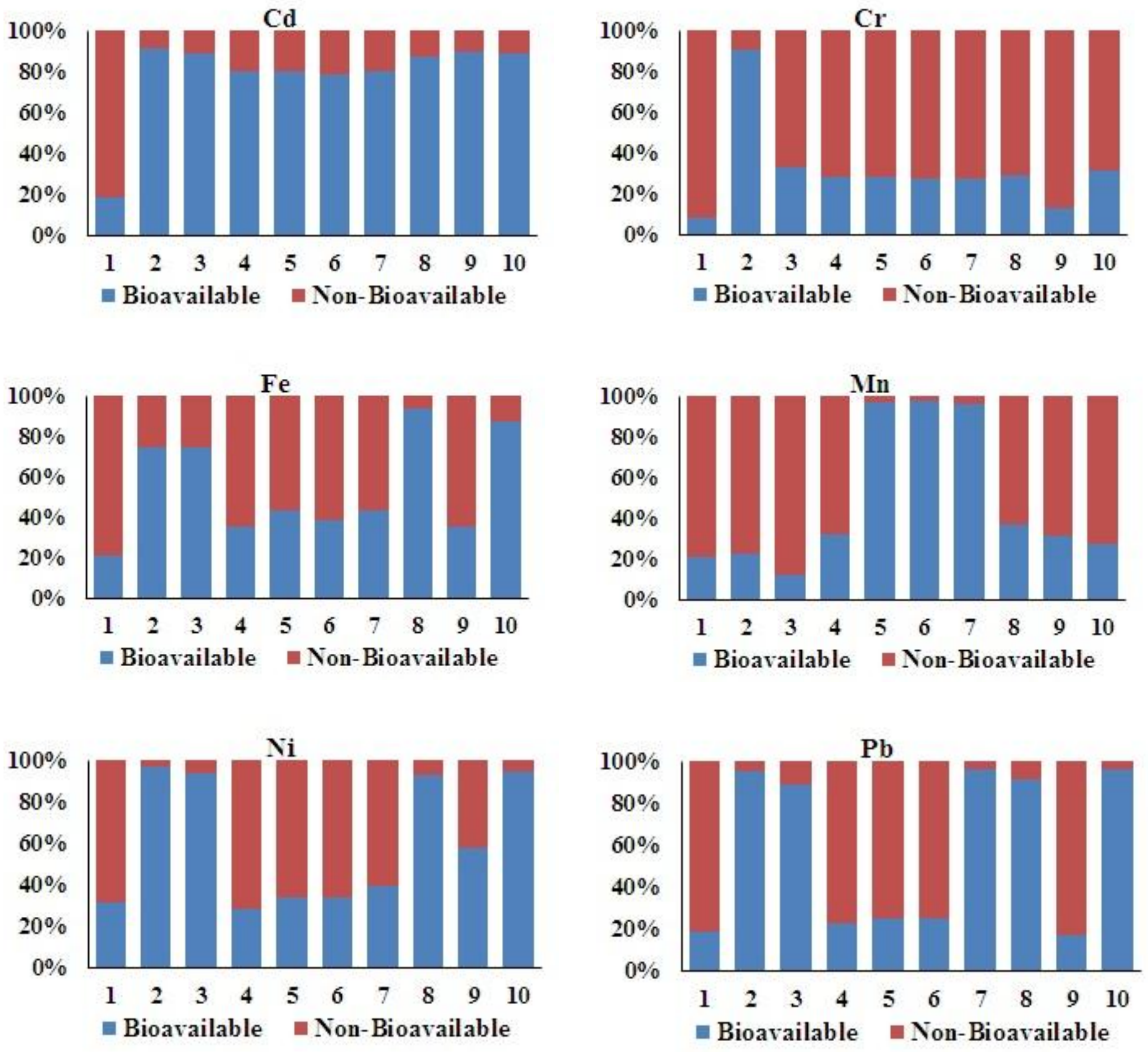

Fig.4. Percentages of metals (%) in the bioavailable and nonbioavailable fractions of sediments from the Great Bitter Lake.

3.5. Assessment of ecological risk

Several approaches have been established and adjusted for the valuation of possible environmental risk **(Brady *et al.*, 2015).** The most prominent way of appraising metal contamination and environmental risk is by computing contamination factor (Cf) of single metals in addition to their enrichment factor (Ef) and geoaccumulation (Igeo) **(El Nemr et al., 2016)**. Up till now, since metals are most possibly to have synergistic properties in the ecosystem, these single metal indices might be inadequate in the evaluation of pollution and risk (**Duodu *et al.*, 2016).** Multimetal indices, e.g. modified risk assessment code **(Saeedi and Jamshidi- Zanjani 2015),** global contamination factor (GCF) **(Ikem *et al.*, 2003),** modified potential ecological risk index (RI-A)

(Hakanson 1980; Liu *et al.*, 2018), and the mean PEL quotient (mPELQ) **(Long and MacDonald, 1998)** can consider the synergistic effects of diverse heavy metals.

3.5.1. Ecological risk of metals based on the total metal contents

Numerical SQGs were utilized to judge the potential environmental significances of heavy metals and to conduct ecological risk assessments **(Naji and Sohrabi, 2015).** Threshold effects level (TEL) and probable effects level (PEL) are SQGs which are extensively utilized to assess the total metal contents in sediments (**MacDonald *et al.*, 1996)**. The TEL and PEL values were recorded in Table 2. TEL is the level below which opposing biological effects rarely occur; PEL is the level above which opposing biological effects regularly take place.

When related to the TEL-PEL SQGs, the contents of Cd, Cr, Ni, and Pb are lesser than the PEL value at 100% of sampling sites. On the other hand, in case of Cr and Pb, 100% of samples are lesser than TEL values, demonstrating that the opposing effects on the aquatic organisms are infrequently occur. In case of Ni, 60% of samples fall in the range between TEL and PEL at sites 2, 3, 4, 6, 8, and 10, signifying that Ni in sediments from the Bitter lake may be infrequently projected to produce opposing toxic effects on biota. Whereas, the contents of Cd are between the TEL value and the PEL value at all sampling sites, so the unbeneficial effect may take place infrequently on biota.

Since metals exist in sediments as complex mixtures, the mean PEL quotient has been performed to define the probable biological consequence of integrated toxicant groups by computing the mean quotients for an enormous range of pollutants by the subsequent equation **(Long *et al.*, 1995)**:

$$mean\ PELQ = \sum_{i=1}^{n} \frac{[C_i\ /PEL_i]}{n}$$

where C_i and PEL_i are the concentration and PEL of pollutant i, respectively, and n is the number of pollutants involved in the estimation. Consequent classification of sites of probable risk has been suggested by **Long and MacDonald (1998)** (Table 3).

The mPELQ considered for sampling sites based on metals (Cd, Cr, Ni, and Pb) are displayed in Table 4. All sites are classified as slightly toxic and deliberated as low to medium priority of potential concern (0.11<mPELQ<1.5).

Table 3. Categorization and values of potential risk relative to E_r^i (Hakanson, 1980), IR thresholds (Liu et al., 2018) and mean PEL quotient (Long and MacDonald, 1998)

	Value	Categorization	Results of the Bitter Lakes
mPELQ	m-PEL-Q<0.1	lowest priority	
	0.11<mPELQ<1.5	medium low priority	Medium low priority
	1.51<mPELQ<2.3	medium high priority	
	mPELQ>2.3	high priority	
E_r^i threshold	<40	Low risk	Cr, Mn, Ni, Pb
	40-80	Moderate risk	-
	80-160	Considerable risk	-
	160-320	High risk	Cd
	>320	Very high risk	-
$E_r^i - A$ threshold	<40	Low risk	Cr, Mn, Ni, Pb
	40-80	Moderate risk	Cd
	80-160	Considerable risk	-
	160-320	High risk	-
	>320	Very high risk	-
RI threshold	<100	Low risk	-
	100-200	Moderate risk	Moderate risk
	200-400	Considerable risk	-
	>400	Very high risk	-
RI-A threshold	<100	Low risk	Low risk
	100-200	Moderate risk	
	200-400	Considerable risk	
	>400	Very high risk	

The potential ecological risk index (RI) expressed by **Hakanson in 1980** is utilized here to evaluate the level of environmental risk of metals in sediment **(Hakanson *et al.*, 1980)**. The RI measures the collective ecological and environmental toxicity to afford a complete estimation of the probable risks of heavy metal contamination, and is calculated as follows:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \; C_f^i$$

$$C_f^i = \frac{C_s^i}{C_n^i}$$

where E_r^i is the potential ecological risk factor of metal i, T_r^i is the toxic response factor of metal i, C_f^i is the contamination factor of metal i, C_s^i and C_n^i is the measured and background level of metal i in sediments, respectively. The coefficients analogous to the toxicity of metals are as follows: Cd = 30, Pb and Ni = 5, Cr = 2, Mn = 1

(Hakanson, 1980; *Xu et al.*, 2008). Owing to the absence of related baseline concentrations of metals for the Bitter Lakes, the average shale levels **(Turekian and Wedepohl 1961)** are designated as the baseline concentrations in this work. The standards utilized for risk classification are registered in Table 3.

The results of E_r^i are obtained in Table 4, according to E_r^i, all metals, except Cd, shows a slight risk at each site, with an E_r^i value of< 40. Elevated E_r^i values for Cd are calculated at sites (2, 3, 5, 7, 8, 9, and 10) demonstrating a maximum risk level, whereas, at other sites, it displayed slight (site 1), or significant (sites 4 and 6), degrees of risk, signifying the dominant contribution and the ecological risk priority of Cd.

3.5.2. Ecological risk of metals based on bioavailable fractions contents

It is obvious from the outcomes of the fractionation scheme that metals in the sediments are associated to diverse forms with various strengths. The strength patterns may consequently give a precise suggestion of sediment reactivity, which consecutively evaluate the risk associated with the existence of metals in an aquatic ecosystem **(Jain, 2004)**.

Table 4. The mean PEL quotient and potential ecological risk index of Cd, Cu, Fe, Mn and Pb, in the Great Bitter Lake sediments

Sites	mPELQ	E_i^r					RI	$E_i^r - A$					RI-A
		Cd	Cr	Mn	Ni	Pb		Cd	Cr	Mn	Ni	Pb	
1	0.12	75	0.1	0.1	0.7	1.7	77.5	14	0.01	0.05	0.21	0.32	14.58
2	0.42	205	0.8	0.2	2.2	7.2	215.5	74	0.71	0.05	2.17	6.86	83.78
3	0.43	215	0.6	0.2	2.4	7.5	225.7	64	0.20	0.06	2.24	6.62	73.12
4	0.23	143	0.2	0.2	1.3	3.4	148.1	20	0.07	0.08	0.36	0.76	21.27
5	0.22	167	0.3	0.2	0.8	4.5	172.7	20	0.09	0.53	0.26	1.12	22
6	0.27	138	0.5	0.2	1.4	3.9	143.9	22	0.13	0.50	0.47	1.16	24.26
7	0.27	178	0.3	0.2	1.1	6.2	185.9	20	0.09	0.56	0.45	5.95	27.05
8	0.37	215	0.4	0.2	2.0	6.9	225.2	63	0.12	0.15	1.82	6.35	71.44
9	0.23	165	0.2	0.2	1.0	4.9	171.2	44	0.02	0.05	0.56	0.81	45.44
10	0.38	224	0.6	0.2	1.9	6.2	232.9	74	0.19	0.07	1.76	5.91	81.94
Min	0.12	75	0.1	0.1	0.7	1.7	77.5	14	0.01	0.05	0.21	0.32	14.58
Max	0.43	224	0.8	0.2	2.4	7.5	232.9	74	0.71	0.56	2.24	6.86	83.78
Average	0.29	172.6	0.4	0.2	1.5	5.2	179.9	41.5	0.16	0.21	1.03	3.59	46.49

To highlight the significance of the metal content in the bioavailable fractions such as acid soluble fractions (Exchangeable + carbonates), Liu *et al.* **(2018)** suggested the usage of these fractions as a replacement for of total contents as enshrined in the C_s^i value. At that time, the estimated E_r^i values are termed E_r^i –A, and the RI values of each site are termed RI-A. Categorizations of $E_r^i - A$, and RI-A are offered in Table 3.

The RI-A values for the Great Bitter Lake ranged between 14.60 and 83.78 (Table 4), designating that all sites are categorized as a slight risk. Matched with original RI, the much lower levels of RI-A originate from the decline of E_r^i for individual metals (Table 4), since the content in the bioavailable fractions, accounted for a part, or even a small part, of the total concentration in the sediments.

Moreover, the amount of ecological risk related to heavy metals might be appraised as a function of their retention by measuring the contamination factors of metals **(Nemati *et al.*, 2009)**. Consistent with **(Saleem et al., 2015),** elevated contamination factor denotes slight retention time and great effect on the aquatic ecosystem. Individual contamination factors (ICF) for sampling sites are calculated from data of the fractionation profile by dividing the concentration of non-resistant fractions by the residual fraction for each site. The global contamination factor (GCF) for each site is estimated by summing the ICF acquired for the metals examined **(Ikem *et al.*, 2003)**. The ICF and GCF are deliberated using the subsequent formula:

$$ICF_{metal} = \frac{C_{non-resistant}}{C_{resistant}}$$

$$GCF = \sum_{i=1}^{n} ICF$$

According to Ikem et al. (2003), ICF designates the risk of pollution by a particular metal, whereas the GCF signifies the integrated probable risks of metals to the ecosystem **(Chen *et al.* 2013)**. ICF and GCF categorizations are described as suggested by Zhao *et al.* **(2012)** as shown in Table 5.

Individual and global contamination factors for Cd, Cr, Fe, Mn, Ni, and Pb in sediments are presented in Table 6. The maximum levels of ICF for Cd, Fe and Ni are shown at sites 2, 3, 8, and 10, Cr at sites 2, and 3, Mn at sites 5, 6 and 7, and Pb at sites 2, 7, 8 and 10. The discrepancies among contamination factors at different sites could be correlated to physicochemical factors that regulate the speed of adsorption and desorption of metals. Generally, the maximum risk from metals considered is calculated at sites 2, 3, 8, and 10. Average ICF values in sediments of the Great Bitter Lake follow the sequence Mn > Pb > Ni > Fe> Cr> Cd. Therefore, Fe, Mn, Ni, and Pb have considerable risk ($3 < ICF < 6$), while Cr expose a moderate risk ($1 < ICF < 3$), and Cd has low risk ($ICF < 0$).

The global contamination factor evaluated from ICF values demonstrated that sites 2, 3, 5, 6, 7, 8, and 10 are greatly affected by heavy metal contaminants ($GCF > 24$).

GCF is an essential indicator as it reveals the integrated probable hazards produced by the toxic metals **(Ikem *et al*., 2003).**

Table 5. Categorization and values of individual (ICF) and global contamination factors (GCF) and risk (RAC) and modified risk assessment codes (mRAC).

	Value	Categorization	Results of the Bitter Lakes
Risk Assessment Code (RAC)	<1	No risk	-
	1-10	Low risk	Cd
	11-30	Medium risk	Cr, Fe, Mn, Ni, Pb
	31-50	High risk	-
	>50	Very high risk	-
Modified risk assessment Code (mRAC)	<1	No potential adverse effect	-
	1≤mRAC<10	Low potential adverse effect	Low potential adverse effect
	10≤mRAC<30	Medium potential adverse effect	
	30≤mRAC<50	High potential adverse effect	
	mRAC≥50	Very high potential adverse effect	-
			-
Individual contamination factor (ICF)	<0	Low risk	Cd
	1 < ICF < 3	Moderate risk	Cr
	3 < ICF < 6	Considerable risk	Fe
	ICF > 6	High risk	Mn, Ni, Pb
Global contamination factor (GCF)	<6	Low risk	-
	6 < GCF < 12	Moderate risk	-
	12 <GCF < 24	Considerable risk	-
	GCF > 24	High risk	High risk

The results recognize that those sites located nearby agricultural, municipal, and industrial areas have high probable risk to the lake ecosystem. However, the metals bioavailability from sediment to the overlying water may be affected by specific parameters as pH, fractions of metals, and the physicochemical characters of the water column **(Ikem *et al*., 2003).**

This work also involved the risk assessment code (RAC), additional multi element index to evaluate the possible effect of metal pollution of the Bitter Lakes. This index is one of the predominant indices to scrutinize mobilization of metals. The RAC model evaluates the ecological risk of metals by considering the proportions of metals in the exchangeable and carbonates forms since metals in these forms are weakly bound and easily bioavailable **(Singh *et al.* 2005; Martin *et al.* 2015).** In this work, RAC is calculated as a function of bioavailable metal levels as expressed by the proportions of the exchangeable (F1) and carbonates (F2) chemical fractions. RAC was calculated using the following formula:

$$RAC_i(\%) = F_1(\%) + F_2(\%)$$

While, RAC does not consider the toxic effects of metals in evaluating the ecological hazards, the modified risk assessment code (mRAC) is designed to categorize toxic effects and accumulation of the produced hazard in a single index **(Saeedi and Jamshidi- Zanjani 2015)**. The mRAC was calculated using the following equation:

$$mRAC = \frac{\sum_{i=1}^{n} T_r^i \ x \ RAC_i}{\sum_{i=1}^{n} T_r^i}$$

where T_r^i is toxicity coefficient of that metal according to Hakanson **(1980)**, and n is the number of metals. The categorization of mRAC is clarified in Table 5.

The outcomes of RAC for the examined metals are offered in Table 6. RAC values are in the range of 4.19-13.44% for Cd, 3.33-13.37% for Cr, 6.30-39.42% for Fe, 6.80-16.36% for Mn, 10.17-22.61% for Ni, and 7.61-22.11% for Pb. Consistent with RAC values, risk level of metals in sediments from the Great Bitter Lake can be arranged in the following sequence Fe>Ni>Pb>Cr>Mn>Cd. Amongst the metals, Cd displays the lowermost risk level. The mean values of RAC for Fe, Ni, Pb, Cr and Mn propose a medium risk level of these metals in the Bitter Lakes sediments.

The results of mRAC index are presented in Table 6. The results exhibit a medium potential risk in a lot of sites (2, 3, 8, and 10) situated nearby Abu Sultan power station and close to the outlet of Malaria Drain. Moderate quantities of mRAC at these sites expose that studied metals can be readily leached to the overlying water through fluctuations in physicochemical circumstances of the ecosystem **(Soliman *et al.*, 2018).**

Agreeing to the results of ecological risk assessment, sampling site 2 suffer from the greatest severe metal pollution, particularly for Ni and Pb, and display elevated ecological risk. The highest value of GCF (61.19), mRAC (14.7) and mRI (83.8) are a reported at this site, which displayed a moderate or significant degree of pollution. The pollution may be accredited to local point sources. Since site 2 is situated adjacent to the electricity station of Abu Sultan, may cause more severe contamination and lead to the high values of metals.

The empirical SQGs and E_r^i evaluate the pollution through data of the total metal contents, while the RAC code, mRAC, ICF, and E_r^i –A valuation explores the metal toxicity and bioavailability. For example, Cd concentration surpasses the TEL and ER values at all sites, consequently being categorized as high risk. But it was mostly dominated by the residual fraction designating a slight reactivity in the lake ecosystem, and consequently show slight risk owing to the RAC, ICF, and $E_r^i - A$ indices. These outcomes designate that the usage of the empirical SQGs thresholds and the potential ecological index for Cd to appraise the ecological risk is inadequate.

Table 6. Risk assessment code (RAC), Individual (ICF) and global (GCF) contamination factors of Cd, Cu, Fe, Mn and Pb, in the Great Bitter Lake sediments

Sites	ICF						GCF	RAC						mRAC
	Cd	Cr	Fe	Mn	Ni	Pb		Cd	Cr	Fe	Mn	Ni	Pb	
1	0.23	0.09	0.27	0.27	0.46	0.23	1.55	8	3.33	6.79	7.76	10.17	8.57	7.8
2	0.56	9.73	2.90	0.29	28.92	18.78	61.19	13.17	34.18	26.92	13.34	22.61	17.73	14.7
3	0.42	0.50	2.97	0.14	14.14	7.84	26.01	13.02	10.84	32.47	6.80	22.43	16.71	12.5
4	0.16	0.39	0.54	0.48	0.39	0.29	2.26	5.59	10.31	19.70	16.36	10.92	10.62	7.9
5	0.14	0.40	0.77	33.56	0.50	0.33	35.70	4.19	12.24	6.30	13.16	14.37	9.34	6.4
6	0.19	0.38	0.64	38.01	0.51	0.33	40.06	6.52	13.06	10.00	14.81	12.73	8.84	8.3
7	0.13	0.38	0.78	26.82	0.65	22.24	50.99	5.06	12.59	8.26	13.87	13.50	22.11	8.6
8	0.41	0.41	15.43	0.63	13.78	10.66	41.32	13.44	13.37	39.42	7.64	22.56	17.22	13.1
9	0.36	0.15	0.54	0.46	1.36	0.20	3.07	5.45	5.07	10.69	13.32	19.70	7.61	6.8
10	0.49	0.46	7.08	0.38	16	26.03	50.45	12.95	9.33	35.31	8.66	21.96	18.25	12.8
Min	0.13	0.09	0.27	0.14	0.39	0.20	1.55	4.19	3.33	6.30	6.80	10.17	7.61	6.4
Max	0.56	9.73	15.43	38.01	28.92	26.03	61.19	13.44	34.18	39.42	16.36	22.61	22.11	14.7
Average	0.31	1.29	3.19	10.10	7.67	8.69	31.26	8.74	12.43	19.59	11.56	17.09	13.70	9.9

Therefore, the combination of diverse indices provides us a comprehensive understanding of metal risks in the sediments and should be performed cautiously to acquire clear assumptions on the toxicity and bioavailability of metal contaminants.

3.6. Source apportionment and association of metals among the various fractions

Pearson correlation analysis was performed to examine the origin of metals and the effect of sediment features. Pearson's correlation coefficients among the total contents of metals and sediment physicochemical properties are reported in Table 7. There are strong positive associations among the contents of Cd, Cr, Fe, Ni, and Pb, which proposes an identical origin input with analogous distribution **(Yang *et al.*, 2009)** and that these metals have comparable properties during transport in the lake ecosystem.

Grain size is one of the influences affecting the baseline levels of metals in sediments **(Zhang *et al.*, 2001).** Both sand and silt sized fractions considerably affect the metal distributions, with negative relationships between sand and Cd, Cr, Fe, Ni, and Pb ($r = -0.758, -0.889, -0.812, -0.949$, and -0.736, respectively) and positive correlations between silt and Cd, Cr, Fe, Ni, and Pb ($r = 0.781, 0.830, 0.761, 0.889$, and 0.722, respectively) (Table 7). The negative correlation of sand designates that these metals may be readily leached by the ion exchange processes owing to the electrostatic interaction of heavy metals as they are weakly bound and is bioavailable to the liquid phase **(Morillo *et al.* 2004).** Fine grained fractions have a tendency to have comparatively maximum metal contents due to the great specific surface area of fine particles.

This enrichment is mostly owing to surface adsorption and ionic attraction **(McCave,1984; Horowitz and Elrick, 1987).** Thus, metal levels display homogeneous distribution tendency to that of silt contents. Furthermore, strong relationship ($p <0.01$) are shown between TOC and almost all metals, as organic matter has a considerable influence on sorption and formation of metals complexes in aquatic sediments **(Passos *et al.* 2010; Samhan *et al.* 2014).** The strong association ($p < 0.01$) among TOC and silt content designates that fine grained fractions deposition may be an important controlling factor on the distribution of TOC in the lake sediments. The negative relationship of carbonates content with Cd ($r = -0.321$), Fe ($r = -0.442$), and Ni ($r = -0.322$) designates that these metals are scarcely bound to carbonates **(Hu *et al.*, 2011).** In contrast, Mn does not associate with other metals, clay, sand, and TOC, proposing that it may have dissimilar sources and is not affected by the sediment properties.

Table 7. Pearson's correlation matrix for the variables of Total (T) Cd, Cr, Fe, Ni, Mn, and Pb and chemical physicochemical characteristics of sediments from the Great Bitter Lake.

	Cd	Cr	Fe	Mn	Ni	Pb	TOC	TCO_3	TP	IP	OP	Sand	Silt	Clay
Cd	1													
Cr	0.75**	1												
Fe	0.73*	0.85**	1											
Mn	0.91**	0.89**	0.77**	1										
Ni	0.79**	0.88**	0.75**	0.96**	1									
Pb	0.94**	0.77**	0.63*	0.92**	0.82**	1								
TOC	0.81**	0.79**	0.76**	0.93**	0.92**	0.79**	1							
TCO3	-0.32	-0.19	-0.44	-0.32	-0.32	-0.17	-0.59	1						
TP	0.78**	0.88**	0.78**	0.93**	0.97**	0.78**	0.88**	-0.38	1					
IP	0.79**	0.86**	0.68*	0.87**	0.83**	0.75**	0.85**	-0.39	0.86**	1				
OP	0.50	0.59	0.61	0.67*	0.78**	0.54	0.61	-0.23	0.81**	0.39	1			
Sand	-0.76*	-0.88**	-0.81**	-0.94**	-0.95**	-0.72*	-0.92**	0.42	-0.95**	-0.89**	-0.69*	1		
Silt	0.78**	0.85**	0.76**	0.92**	0.89**	0.71**	0.92**	-0.47	0.89**	0.90**	0.57	-0.98**	1	
Clay	0.29	0.67*	0.60	0.52	0.70*	0.39	0.47	-0.02	0.70*	0.38	0.82**	-0.59*	0.40	1

Correlation is significant at $P < 0.05$, $P < 0.01$; n = 10.

Table 8. Pearson's correlation matrix for total (T), resistant (R) and nonresistant (NR) Cd, Cr, Fe, Mn, Ni and Pb in sediments of the Great Bitter Lake.

	TCd	TCr	TFe	TMn	TNi	TPb	NRCd	NRCr	NRFe	NRMn	NRNi	NRPb	RCd	RCr	RFe	RMn	RNi	RPb
TCd	1																	
TCr	0.75**	1																
TFe	0.73*	0.85**	1															
TMn	0.91**	0.89**	0.77**	1														
TNi	0.79**	0.88**	0.75**	0.96**	1													
TPb	0.94**	0.77**	0.63*	0.92**	0.82**	1												
NRCd	0.83**	0.77**	0.72*	0.93**	0.86**	0.79**	1											
NRCr	0.45	0.83**	0.64*	0.63*	0.66*	0.56	0.63*	1										
NRFe	0.87**	0.82**	0.84**	0.93**	0.87**	0.82**	0.91**	0.54	1									
NRMn	-0.11	-0.11	-0.22	-0031	-0.38	-0.08	-0.55	-0.24	-0.31	1								
NRNi	0.81**	0.84**	0.77**	0.96**	0.95**	0.83**	0.95**	0.67*	0.93*	-0.45	1							
NRPb	0.83**	0.76**	0.57	0.89**	0.83**	0.91**	0.77**	0.58	0.83**	-0.14	0.85**	1						
RCd	0.88**	0.53	0.53	0.65*	0.51	0.82**	0.46	0.21	0.63*	0.29	0.47	0.66*	1					
RCr	0.57	0.41	0.45	0.53	0.47	0.34	-0.17		0.54	0.19	0.39	0.39	0.61	1				
RFe	-0.85**	-0.67*	-0.61*	-0.89**	-0.81**	-0.81**	-0.88**	-0.42	-0.95**	032	-0.88**	-0.86**	0.56*	-0.51	1			
RMn	0.37	0.33	0.44	0.57	0.66**	0.39	0.58	0.16	0.55	-0.71*	0.7**	0.46	0.09	0.31	-0.53	1		
RNi	-0.63*	-0.53	-0.58	-0.71*	-0.60	-0.64*	-0.86**	-0.49	-0.78**	0.55	-0.82**	-0.67*	-0.25	-0.14	0.78**	-0.59	1	
RPb	-0.47	-0.49	-0.35	-0.60	-0.58	-0.56	-0.53	-0.44	-0.63*	0.24	-0.64*	-0.84**	-0.29	-0.16	0.69*	-0.46	0.58	1

Correlation is significant at $P < 0.05$, $P < 0.01$; n = 10.

Furthermore, agreeing with **Rubio *et al.* (2000)** correlation statistical analysis is usually implemented to examine the probable relationship found among diverse variables of metals. The relationship among total metals with resistant and nonresistant forms can be utilized to test the amount of lithogenic origin and/or manmade sources of metals studied (Table 8). Total Cd was significantly correlated to resistant Cd ($r = 0.88$, $p < 0.01$) and nonresistant Cd ($r = 0.83$, $p < 0.01$). This designates that once Cd concentrations are increased in the sediment, this is mostly owing to Cd of natural origin and from manmade intrusions. Total Fe, Mn, Ni and Pb are related significantly ($p < 0.01$) to the nonresistant fractions of these metals ($r = 0.84$, 0.84, 0.95, and 0.90, respectively). As mentioned before, this entitles that manmade intrusions not only affect the total metal contents of metals but also their fractionation patterns in the sediment.

CONCLUSION

This work examined the total contents and fractionation profile of metals in the sediments from the Bitter Lakes. The analysis exposed that the concentrations (µg/g, dw) of Fe, Mn, Pb, Ni, Cr, and Cd in sediments fluctuated from 2800-3900, 123.56-495.28, 6.77-29.87, 8.85-32.55, 3.30-35.40, and 0.75-2.24, respectively. Comparatively higher levels of metals were mostly distributed in and nearby agricultural, municipal, and industrial areas. The outcomes also exhibited that the metal fractionation proportions in the residual and Fe/Mn oxides forms are the most considerable, while the exchangeable, carbonate, and organic bound heavy metals are quite low. The extractability pattern of metals in the residual fraction follow the order Cd > Cr > Mn > Fe > Pb > Ni. The increased percentages of total residual fractions regarding nonresidual fractions of Cd, Cr, and Mn proposed that the origins of these metals in sediments may originate largely from natural sources. While, below 50% contribution of other metals in the residual fraction exposed that natural origin is not a main source of these metals in sediments of the Bitter lakes.

The potential ecological risk was appraised using multi-metal indices, such as the modified risk assessment code (mRAC), global contamination factor (GCF), modified potential ecological risk index (RI-A), and the mean PEL quotient (mPELQ).

TEL/PEL guidelines exposed that toxic hazards may happen regularly at some sites in the Bitter Lakes sediments especially from Cd and Ni. According to mPELQ all sites were classified as slightly toxic and deliberated as low to medium priority of potential concern. Potential ecological risk analysis of metal contents designated that Cd had elevated individual potential ecological risk factor E_r^i, while the other metals had low risk at all examined sites. The multi elemental potential ecological risk factor (IR) indicated moderate ecological risk for the investigated metals. The RAC results specified low risk for Cd and medium risk for other metals. The results of ICF and GCF exhibited that sites 2, 3, 5, 6, 7, 8, and 10 had greater GCF values than the other sites designating elevated ecological risk. In terms of ICF values, a decline rank in ecological risk by heavy metals was Mn > Pb > Ni > Fe> Cr> Cd. Consequently, Cd had the lowest risk to the Bitter Lakes ecosystem.

All the risk assessment indices based on the bioavailable fraction concentrations (RAC code, mRAC, ICF, and E_r^i –A) performed in this work exposed an observable slight pollution risk by Cd. Nevertheless, opposing conclusions acquired when different indices based on the total metal contents such as the potential ecological risk factor E_r^i and SQGs are used. These conclusions designated that the application of the empirical SQGs thresholds and the potential ecological index for Cd to assess the ecological risk is inadequate. Therefore, the combination of diverse indices provides a complete understanding of metal risks in the sediments and should be applied cautiously to get clear decisions on management of the lake environment.

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