

## ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER AND SURFACE SEDIMENTS OF THE MAHARLU SALINE LAKE, SW IRAN\*

F. MOORE<sup>1\*\*</sup>, G. FORGHANI<sup>2</sup> AND A. QISHLAQI<sup>3</sup>

Department of Earth Sciences, Faculty of Sciences, Shiraz University, Shiraz, I. R. Iran

<sup>1</sup>Moore@geology.susc.ac.ir

<sup>2</sup>gforghani@gmail.com

<sup>3</sup>Qishlaqi@shirazu.ac.ir

**Abstract** – Maharlu saline Lake is located in the SW of Iran. To assess the environmental pollution of the lake, the total concentrations of As, Cr, Co, Cu, Cd, Pb, Zn, Ni, Fe, and Mn were determined in the surface sediments and water of the lake. As and Cr were not detected in the water samples, however, the mean concentrations of other dissolved metals in Maharlu Lake water were 0.28 mg/l for Cu, 0.28 µg/l for Cd, 5.17 µg/l for Pb, 0.37 mg/l for Zn, 2.36 µg/l for Ni, 2.88 µg/l for Co, 10.4 mg/l for Fe, and 1.5 mg/l for Mn. Different water and sediment quality assessment approaches indicated that in this lake, metals can be divided into three different groups: (a) Co, Pb, and Cd. These metals have the highest enrichment factors (the mean values are 35.8, 76.9, and >36.6, respectively), geoaccumulation indexes (the mean values are >3), and contamination factors (11.1, 29, and 8, respectively) compared with other studied elements; thus, the Maharlu Lake is highly polluted with these metals, and they are mainly from anthropogenic sources; (b) Cu, Zn, and Ni. Their mean enrichment factor values are 6.6, 3.4, and 6, respectively; their mean geoaccumulation indexes are <1, and their mean contamination factor values are 2, 1.1, and 2, respectively. The enrichment factor of these metals is higher than 10 only north of the lake. The Maharlu Lake is moderately polluted with these metals, and they are from both natural and anthropogenic sources; (c) Cr, As, Fe, and Mn. These elements have the lowest mean enrichment factor (1, 3.5, 2, and 4.2, respectively), geoaccumulation indexes ( $\leq 0$ ), and contamination factor (0.32, 0.91, 0.63, and 1.5, respectively) values; thus the Maharlu Lake is not polluted with these elements, and they are mainly from natural sources. Results indicated that the Maharlu Lake sediments have a high contamination degree (56.66). Comparisons with consensus-sediment quality guidelines reveal that Ni and Pb pose the greatest environmental threat to aquatic organisms. In order to protect the lake from further contamination, the treatment and recycling of wastewaters discharged into the lake is needed.

**Keywords** – Environmental assessment, geochemical calculations, Iran, Maharlu saline Lake, sediment quality

### 1. INTRODUCTION

Lakes can be readily contaminated by human activity without any obvious signs [1], thus they have long attracted scientific and environmental interest. Among the various pollutants, heavy metals are the most toxic, persistent, and abundant that can accumulate in aquatic habitats and their concentration increases through biomagnification [2, 3, 4]. The most toxic heavy metals Cr, Ni, Pb, Cd, and As. Cr (VI), Ni and Cd are carcinogenic; As and Cd are teratogenic, and the health effects of Pb include neurological impairment and malfunctioning of the central nervous system [5, 6]. Although some heavy metals such as Fe, Mn, Co, Cu, and Zn are essential micronutrients for fauna and flora, they are dangerous at high levels [6, 7, 8]. Thus, for organisms living in lakes, elevated essential and non-essential heavy metal content may impart a significant impact on health, reproduction, and survival. Contaminants may eventually pass

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\*\*Corresponding author

through the food chain to human and result in a wide range of adverse effects. Heavy metals are natural constituents of lake waters, and some of the essential ones are present at low concentrations. However, during the last few decades, rapid expansion of human activity has continuously accelerated the risk of environmental pollution with heavy metals. Distinguishing the anthropogenic inputs from the natural ones is the basis of environmental management [9]. Heavy metals discharging into a lake from both natural and anthropogenic sources are distributed between bed sediments (as sink and source of heavy metals) and aqueous phases. Thus, in evaluating the pollution condition of a water body, both sediments and water should be considered [10].

The Maharlu Lake, located 23 Km southeast of Shiraz, SW Iran, is an important habitat for artemia and various birds. Due to declining water quality, increased mortality rate, and eventual desertion of immigrant birds, this lake has recently been the subject of heated debates. The reason for the deterioration of the quality of water is discharge of industrial and urban wastewaters through a seasonal river (Khoshk River), along with various drainages into the north of the lake. The Khoshk River, as the main tributary of the Maharlu Lake, passes through Shiraz city. During the last three decades, rapid urbanization and industrialization of Shiraz has increased the pollution load and accelerated the contamination of river water [11]. Some possible anthropogenic sources of heavy metal contamination in the Maharlu Lake watershed include paint factories, electronic production facilities, building material, municipal landfill, and untreated urban wastewaters.

Figure 1 shows the geological position of Maharlu Lake. The average length and width of the lake are about 31 and 11 km, respectively. Carbonate and evaporate units from Eocene-Oligocene time surround the Lake. Some salt diapirs representing the oldest rocks in Iran (Late Proterozoic Hormoz Formation) cut across carbonatic anticlines and synclines south and east of the lake, and significantly increase the salinity of the lake water ( $EC > 10000$  mS/cm).

In this study, the concentration of As, Pb, Cu, Zn, Cr, Fe, Mn, Ni, Co, and Cd in the water and sediments (surface and subsurface) of Maharlu saline Lake (SW Iran) is investigated. Some of the important limnological parameters including pH, EC, temperature, and the concentration of major cations and anions are also presented. The main aims of this study were:

1. determining background concentrations of the investigated heavy metals
2. assessing the water and surface sediment contamination by heavy metals and prioritizing contaminated areas for further investigation
3. distinguishing between natural and anthropogenic sources of the studied metals

The results of this study can be used by authorities for directing environmental monitoring, management, and remediation programs.

## 2. MATERIALS AND METHODS

### a) Sampling

In April 2005, twelve samples of water and surface and subsurface sediments were collected from the following sampling points: Khoshk River discharging point (sampling sites  $M_1$ ,  $M_2$ , and  $M_3$ ), west and east of the lake (sampling sites  $M_4$ - $M_9$ ), and the center of the lake (sampling sites  $M_{10}$ ,  $M_{11}$ , and  $M_{12}$ ). Figure 1 displays the location of the sampling points. The pH, temperature, and electrical conductivity (EC) of water were measured in situ. Water samples were collected in 1 L new PE bottles. Surface sediments (top 5cm) were sampled using a Van Veen grab sampler, and then transferred into polyethylene bags. The water and sediment samples were then kept in an icebox before being prepared for analysis.

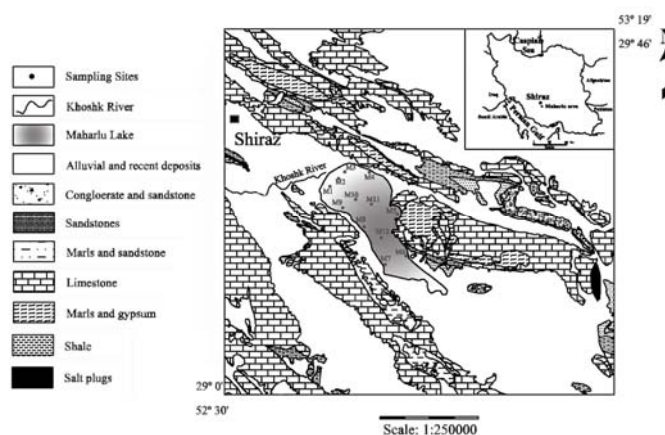


Fig. 1. Geological map of Maharlu saline Lake showing the location of sampling sites

The 'background concentration' of heavy metals is very important and useful for determining the anthropogenic impact on the aquatic ecosystems. In lake sediments, the background concentration mainly comes either from the watershed soil or the parent rock [9]. The deep sediments with relatively low concentrations of pollutants may also be considered as background composition [12]. In this study, both soils surrounding the lake and deep sediment samples were analyzed in order to find the best local background composition. Soil and background samples were also used for determining the sources of elements and thus, for distinguishing between their natural and anthropogenic inputs. For this purpose, five deep sediment samples (2 meter deep) were collected 50 meters from the NE, W, E, and S of the lake banks. In choosing deep sampling points, care was taken to choose areas least disturbed by anthropogenic interferences such as rural settlements or agricultural activities. The deep samples were taken using a hand auger and then were mixed to obtain a composite sample representing background concentration. Twelve topsoil samples (the upper 3 centimeters) were collected from the north and west banks simply by scooping using a plastic spade. In each sampling point, soil samples were also taken as bulk samples from approximately 1m<sup>2</sup> surface areas. Soil samples were put into plastic sealed bags and transferred to the laboratory.

#### b) Sample Preparation and Analysis

Soil and sediment samples were air dried, and then, the <63μm size fraction was recovered by sieving. This size fraction is widely used to eliminate the effect of particle size and to obtain a more homogeneous grain distribution [13]. This fraction is also the most chemically active sediment phase consisting primarily of clay and silt particulates [14]. Total trace metal concentrations of soils and sediments were analyzed after digestion with HF-HNO<sub>3</sub>-HClO<sub>4</sub> [15].

Water samples were filtered using a vacuum pump and 0.45μm pore-size filter papers in order to separate particulate matter. The filtered samples were then split into two portions: one portion was acidified with HNO<sub>3</sub> for dissolved element measurement and the second unacidified portion was used for determination of dissolved anions. The samples were kept at 4°C prior to analysis. Heavy metal and major element concentrations were measured using an ICP-OES instrument (JY 2000), Chloride and sulfate concentrations were determined using titration and turbidimetric methods, respectively, and nitrate and phosphate were determined by spectrophotometric methods.

The accuracy and precision of the measurements were checked using SPEX CertiPrep standards (manufactured under UL ISO 9001 Quality Assurance System). Also, replicate measurements of target elements in each sample were carried out and the mean concentrations were reported. Quantification of element concentrations was based upon calibration curves involving standard SPEX solutions.

### c) Data Analysis

Geochemical criteria i.e. enrichment factor ( $EF$ ), geoaccumulation index ( $I_{geo}$ ) defined by Müller [16], contamination factor ( $C_f$ ) of heavy metals, and contamination degree ( $C_d$ ) of sampling sites defined by Håkanson [17] were determined as essential calculations for assessment of sediment pollution. Enrichment factor of heavy metals was calculated as the ratio of elemental concentration of sediment normalized to immobile Al:

$$EF = (C_n/Al)_{\text{sediment}} / (C_n/Al)_{\text{reference}} \quad (1)$$

The geoaccumulation index ( $I_{geo}$ ), was calculated as follows:

$$I_{geo} = \log_2 [C_n / 1.5B_n] \quad (2)$$

Contamination factor was determined as:

$$C_f = C_n / \text{mean } B_n + \text{one } S.D. \quad (3)$$

The contamination degree ( $C_d$ ) was defined as:

$$\text{the sum of all contamination} \quad (4)$$

$C_n$  in the above formulas is the concentration of the examined element 'n' in the surface sediments, and  $B_n$  is the geochemical background concentration of metal 'n'. Authors usually refer to world average shale [18] and / or upper continental crust [19] compositions as reference materials for the assessment of contamination levels [13]. However, these global standards are not always representative of local lithologic anomalies [20, 21]. In this study, values obtained from a local background sample have been taken equal to reference material values in  $EF$  and  $I_{geo}$  calculations; however, total metal concentrations were compared with global reference materials (world average shale, UCC). To place observed metal concentrations into ecotoxicological context, obtained results were compared with consensus-based sediment quality guidelines (SQGs) defined by [22]. SQG values referred to as the threshold effect concentration (TEC) and the probable effect concentration (PEC) provide a reliable basis for assessing sediment quality conditions in aquatic ecosystems. TEC defines values below which harmful effects are unlikely to be observed, while PEC defines values above which harmful effects are likely to be observed [22].

Soil metal concentrations were normalized using upper continental crust (UCC) values.  $EE_{\text{soil}}/EE_{\text{UCC}}$  ratio  $>1$  suggests contamination condition, whereas  $EE_{\text{soil}}/EE_{\text{UCC}}$  ratio  $<1$  reveals that the soil is not contaminated with a particular element (i.e. the metals are of geological origin) [23].

Descriptive data analysis (including mean, standard deviation, maximum, and minimum values) were performed using SPSS 11.5 software.

## 3. RESULTS AND DISCUSSION

### a) Water Chemistry

Table 1 shows some limnological parameters of the Maharlu Lake, as well as chemical composition of lake water. Measured pH values are approximately neutral (7.53-7.72), resulting from carbonatic formations surrounding the lake basin. Due to the high TDS (254.64 g/L) and EC ( $161.5 \times 10^3$  mS/cm), the Maharlu Lake water is not suitable for drinking. The most abundant dissolved constituents of the Maharlu Lake are  $\text{Cl}^-$  (3180.8 mgL<sup>-1</sup>)  $>$   $\text{Na}^+$  (2487.7 mgL<sup>-1</sup>)  $>$   $\text{Mg}^{2+}$  (310.6 mgL<sup>-1</sup>)  $>$   $\text{SO}_4^{2-}$  (154.8 mgL<sup>-1</sup>), thus, the water is Na-Cl type (Figure 2).

Table 1. Main limnological and chemical characteristics of Maharlu saline Lake  
The means and ranges of measured parameters ( $n=12$ ) are reported

Limnological characteristics		Anion concentration		Cation concentration	
Surface area (km <sup>2</sup> )	250	PO <sub>4</sub> <sup>3-</sup> (mg/l)	0.20 (0.03-0.3)	Na <sup>+</sup> (mg/L)	2454.2 (2276.7-2865.6)
Mean depth (m) at wet season	3	SO <sub>4</sub> <sup>2-</sup> ( mg/l)	155.7 (117-201)	Ca <sup>2+</sup> ( mg/L)	53.1 (45-85)
Average annual precipitation (mm)	492	NO <sub>3</sub> <sup>-</sup> ( mg/l)	3.2 (1.9-5.1)	K <sup>+</sup> ( mg/L)	3.5 (3.1-3.9)
Average annual evaporation (mm)	291	Cl <sup>-</sup> (mg/l)	3181.8 (2780-3390)	Mg <sup>2+</sup> ( mg/L)	313.2 (285-350)
pH of water	7.6 (7.53-7.72)	HCO <sub>3</sub> <sup>-</sup> ( mg/l)	3.3 (2.9-4.0)	Fe (mg/L)	10.4 (7.8-11.5)
T (°C)	23.7 (22.7-25)	CO <sub>3</sub> <sup>-</sup> (mg/l)	0.6 (0-1.1)	Mn mg/L)	1.5 (.85-2.0)
EC ( $\times 10^3$ ) (ms/cm)	161(134-164)				
TDS (g/L)	254.9 (226.2-309)				

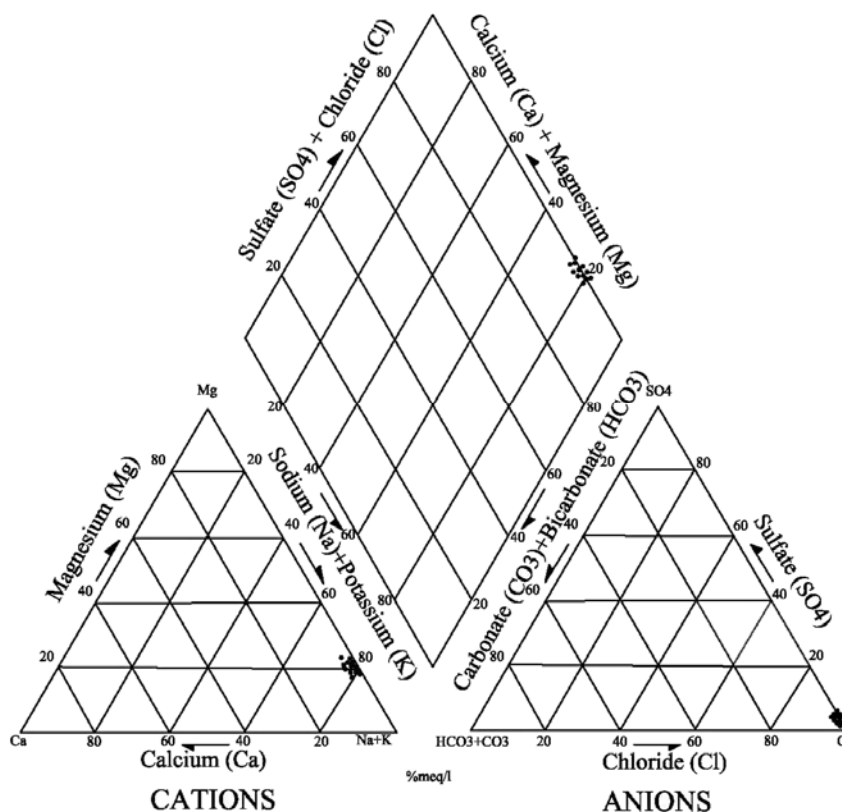


Fig. 2. Piper diagram showing the relative cation and anion compositions of the Maharlu Lake water. This diagram confirms the Na-Cl type for Maharlu Lake water. The filled circles show the composition of 12 analyzed water samples

In general, the mean concentration of NO<sub>3</sub><sup>-</sup> in the water samples of the Maharlu Lake is below the maximum allowable concentration (40 mg/l, Table 1). This may be due to denitrification, since a high load of organic substances, which consume oxygen through denitrification, is transported to the lake.

Phosphate concentration in unpolluted waters typically ranges from 0.01-0.1 mg/l [24]. The mean phosphate content of of Maharlu Lake water (0.21 mg/l, Table 1) exceeds this range. Excess phosphate may be contributed by phosphatic fertilizers used in agricultural lands near the lake.

Dissolved trace element concentrations are generally taken as indicators of the pollution extent in an

aquatic environment. In analyzed samples, As and Cr contents were below instrumental detection limits, perhaps due to their low loading into the lake. The concentration of other analyzed trace metals in the Maharlu Lake water ranges as follows: Cu (0.01-0.47 mg/l), Cd (0.16-0.45 µg/L), Pb (3.6-7.13 µg/L), Zn (0.011-0.61 mg/l), Ni (1.43-2.93 µg/L), Co (1.18-5.18 µg/L), Fe (7.81-11.49 mg/l), and Mn (0.85-1.97 mg/l). The mean values of analyzed trace metals in the Maharlu Lake water are higher than the reported allowable values for fresh water [25] and aquatic life [26] (Table 2). In particular, Ni, Co, Pb and Cd values are high, pointing to anthropogenic loading, probably from Khoshk River discharges and soil runoff.

Table 2. Trace metal concentrations in 12 water samples from the Maharlou saline Lake compared with reference values for freshwater and aquatic life (n.d. means not determined)

Sampling sites	Co (µg/l)	Ni (µg/l)	Zn (mg/l)	Pb (µg/l)	Cd (µg/l)	Cu (µg/l)
M1	5.18	2.93	0.61	7.13	0.42	0.32
M2	4.51	2.82	0.37	6.34	0.45	0.47
M3	2.92	2.55	0.15	4.53	0.32	0.13
M4	3.3	2.77	0.28	4.22	0.3	0.26
M5	2.92	2.5	0.29	3.6	0.28	0.01
M6	3.17	2.42	0.25	3.88	0.3	0.33
M7	2.88	2.47	0.11	5.68	0.29	0.24
M8	1.32	2.34	0.46	5.47	0.26	0.17
M9	1.28	2.8	0.5	5.21	0.19	0.44
M10	3.31	1.64	0.58	5.44	0.24	0.31
M11	1.18	1.64	0.42	5.57	0.17	0.3
M12	2.6	1.43	0.43	5.00	0.16	0.37
Mean value	2.88	2.36	0.37	5.17	0.28	0.28
Reference values for freshwater [25]	5	0.3	0.005	3	2	0.003
Aquatic life concentration [26]	n.d.	0.25	0.03	1	15-25	0.002

### b) Soils Chemistry

The  $EE_{soil}/EE_{UCC}$  ratios  $<1$  for Cu, Zn, Fe, Mn, and Pb show that soils near the lake are not contaminated with respect to these elements (Figure 3). However, all soil samples in the vicinity of the Maharlu Lake are contaminated with Ni, Cr, As, and Cd. Cr and Ni occur naturally in the Earth's crust. However, it is inevitable that the encroachment of the polluted water of Maharlu Lake causes soil contamination. The concentration of Cr in the lake water is below the detection limit, thus Cr mainly comes from natural sources, whereas Ni may either come from natural (structural lattices of soil minerals) and / or anthropogenic (lake water) sources (Maharlu lake water is highly polluted with respect to Ni). The higher average concentration of As in the analyzed soils (6.91mg/kg) compared with upper continental crust composition is probably the result of pesticide application in farmlands rather than lake water, because the concentration of As in the lake water is below the detection limit. Cd is also known to be present in phosphate-rich fertilizer [21]. Thus, in addition to invasion of contaminated lake water, the application of pesticides is another probable source for soil Cd contamination.

Figure 3 indicates that Co contamination occurs in sites close to the lake (especially sampling sites 7 and 8 north of the lake). The results indicate that nearby soil is the probable source (especially for As and Cr) and sink (especially for Ni, Co, and Cd) of heavy metals. Hence, in assessing sediment contamination, it cannot be used as uncontaminated natural reference material.

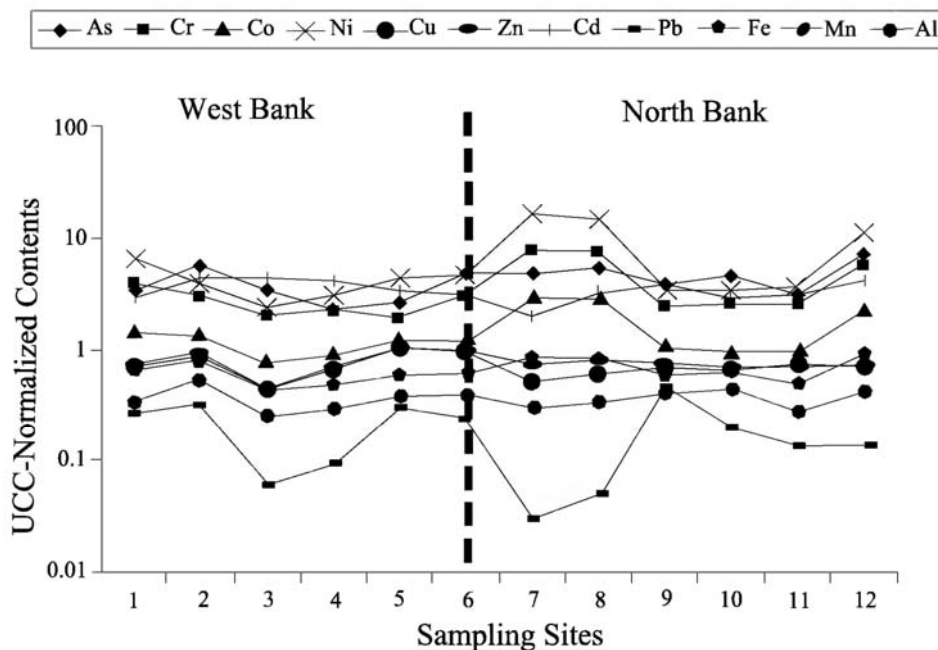


Fig. 3. Multi-elemental normalization diagram for surface soil samples in the vicinity of Maharlu Lake, Metal concentrations are normalized to upper continental crust (UCC) values (from [19])

### c) Sediment Chemistry

The total concentrations (mg/kg) of metals in surface sediments presented in Table 3 range as follows: As (0.36-0.87), Cr (4.57-64.11), Co (48.5-277.8), Ni (100.9-310.8), Cu (19.9-59.7), Zn (37.3-101.4), Cd (1-5.8), Pb (84.3-202.2), Fe (12814-27460), Mn (204-831), and Al (8103-33894). The highest total concentrations of heavy metals occur north of the lake, close to the Khoshk River discharging point.

Table 3. Total metal concentrations (mg/kg) in the <math><63\mu\text{m}</math> sediment fraction for Maharlu Lake sediments, compared with sediment quality guidelines (n.d. means not determined)

Sampling sites	As	Cr	Co	Ni	Cu	Zn	Cd	Pb	Fe	Mn	Al
M1	0.54	43.35	125.7	287.2	59.7	89.8	1.5	119.3	23536	730	11834
M2	0.51	62.45	190	238.8	45.9	87.7	2.1	133.3	20480	640	12734
M3	0.61	57.85	277.8	281.4	46.4	101.4	2.6	146	23857	596	8103
M4	0.48	58.35	119.7	310.8	25.8	44.7	3.0	202.2	20168	831	29670
M5	0.54	51.41	51.5	193.4	21.9	54.4	3.1	173.2	14191	793	33142
M6	0.52	64.11	85.9	206	50.4	71.8	5.7	165.4	27460	574	29374
M7	0.52	32.37	171.5	166	33.5	71.3	5.8	171.5	20353	430	33894
M8	0.41	29.84	224	100.9	19.9	60.3	3.5	156.7	15058	648	12231
M9	0.44	24.35	263.2	171.3	40.0	57.6	4.6	189.4	16758	323	21045
M10	0.46	33.95	98.0	219.4	56.0	81.5	1.0	84.3	23583	375	9325
M11	0.36	19.92	48.5	141.2	30.2	50.5	2.5	200.5	15464	509	22859
M12	0.87	4.57	91.7	167.5	28.0	37.3	2.3	181.4	12814	204	17365
Average values	0.52	40.21	145.62	206.99	38.14	67.35	3.14	160.26	19476.73	554.41	20131
Consensus-based TEC [22]	9.79	43.4	n.d.	22.7	31.6	121	0.99	35.8	n.d.	n.d.	n.d.
Consensus-based PEC [22]	33	111	n.d.	48.6	149	459	4.98	128	n.d.	n.d.	n.d.

Comparison of the values obtained in this study with local and global reference materials indicates that the average concentrations of Cd, Co, and Pb in surface sediments of the Maharlu Lake are higher (Figure 4). Table 3 indicates that all analyzed samples exceed the TEC for Ni, Pb, and Cd, while more than eighty percent of the samples exceed the PEC for Pb and Ni.

The concentration of Cu, Zn, Ni, Mn, Fe, As, and Cr in the Maharlu Lake sediments is either close to, or lower than UCC, average shale, and local background sample. All samples are lower than TEC for As, and nearly forty percent exceed TEC for Cr and Cu. All samples fall below the PEC for As, Cr, Cu, and Zn, and none fall above TEC for Zn.

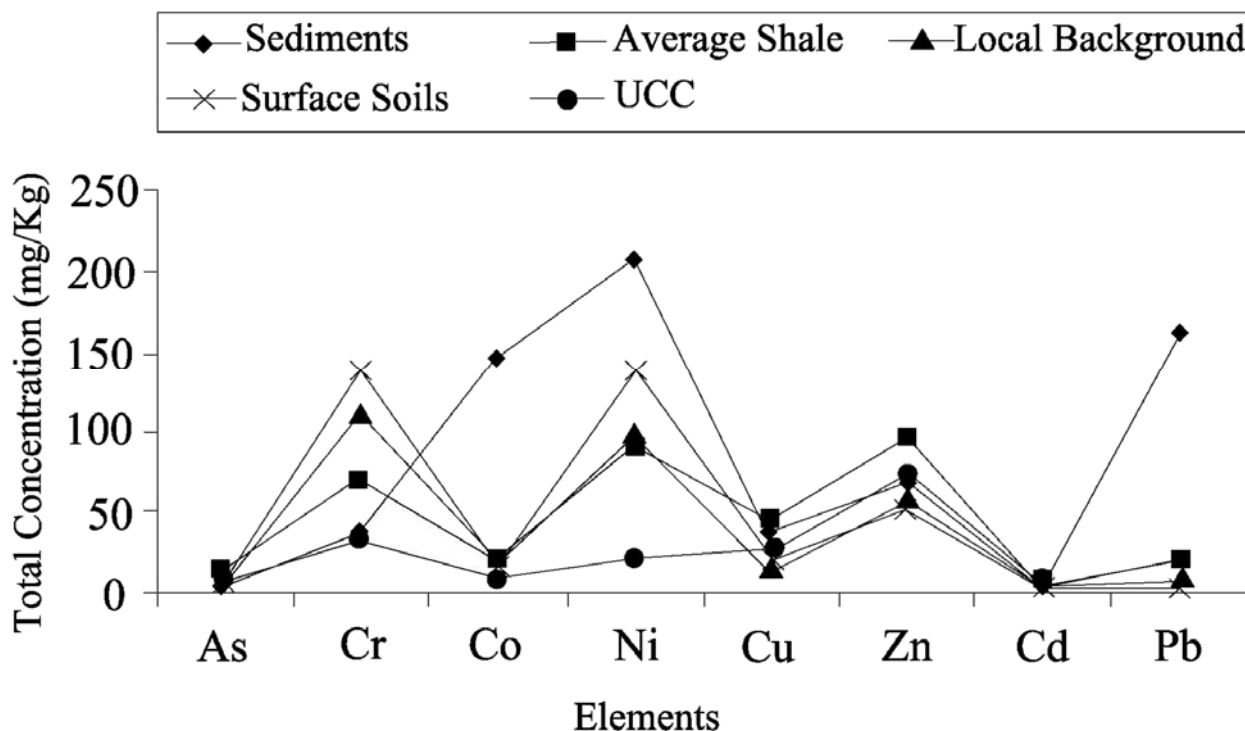


Fig. 4. Average metal concentration of Maharlu lake sediments compared with average shale (from [18]), upper continental crust (from [19]), and nearby soils (this study)

Figure 4 indicates that only Cr, As, and Fe concentrations in sediment samples are lower than nearby soils, while the concentration of Pb, Co, and Cd in surface sediments is much higher than soils. Average concentrations of Ni, Cu, and Zn in the sediment samples are slightly higher than the soil samples. These comparisons indicate that there is an apparent heavy metal pollution risk for the Maharlu Lake, especially with respect to Co, Cd, and Pb; these elements mainly come from the Khoshk River. According to the consensus-based SQGs, adverse biological effects are to be expected for Ni and Pb, and to some extent for Cd. However, nearby soils are also a probable source for heavy metals, especially for As and Cr. Whereas Zn is not associated with any adverse effect, As, Cr, and Cu may have some adverse environmental impacts.

#### d) Geoaccumulation index of heavy metals in surface sediments

Figure 5 shows the range and average values of  $I_{geo}$  values for each metal, using local reference material in the form of box and whisker plot. Based on average values of  $I_{geo}$ , the ranking of intensity of heavy metal pollution of the Maharlu Lake surface sediments is as follows: Pb>Cd>Co>Cu>Ni>Mn>As>Zn>Fe>Cr. Müller [16] has determined seven classes of  $I_{geo}$ : samples may be classified as *unpolluted* ( $0 \leq I_{geo}$ ), *unpolluted to moderately polluted* ( $0 \leq I_{geo} \leq 1$ ), *moderately polluted* ( $1 \leq$



$I_{geo} \leq 2$ ), moderate to strongly polluted ( $2 \leq I_{geo} \leq 3$ ), strongly polluted ( $3 \leq I_{geo} \leq 4$ ), strongly to extremely polluted ( $4 \leq I_{geo} \leq 5$ ), and extremely polluted ( $I_{geo} \geq 5$ ). Figure 6 displays sample percentages in Müller classes for As, Cr, Cu, Cd, Pb, Zn, Ni, and Co. Arsenic, Cr, Fe, Mn, Zn, and Ni concentrations fall mainly in classes 0 and 1. For Pb, samples mainly fall in class 5 (83.33% of total samples) and the remainder 16.66% in class 4. For Cd, 50% of the samples fall in class 4, 25% in class 3, 16.66% in class 5, and 8.33% in class 2. For Co, 83.3% of the samples are included in classes 3 and 4, and the remaining 16.33% fall in class 2. These results indicate that the surface sediments of the Maharlu Lake can be categorized as follows: unpolluted with As, Cr, Zn, Fe, and Mn (average  $I_{geo} < 0$ ), unpolluted to moderately polluted with Cu and Ni ( $0 < \text{average } I_{geo} < 1$ ), moderately to strongly polluted with Co ( $2 < \text{average } I_{geo} < 3$ ), strongly polluted with Cd ( $3 < \text{average } I_{geo} < 4$ ), and strongly to extremely polluted with Pb ( $4 < \text{average } I_{geo} < 5$ ).

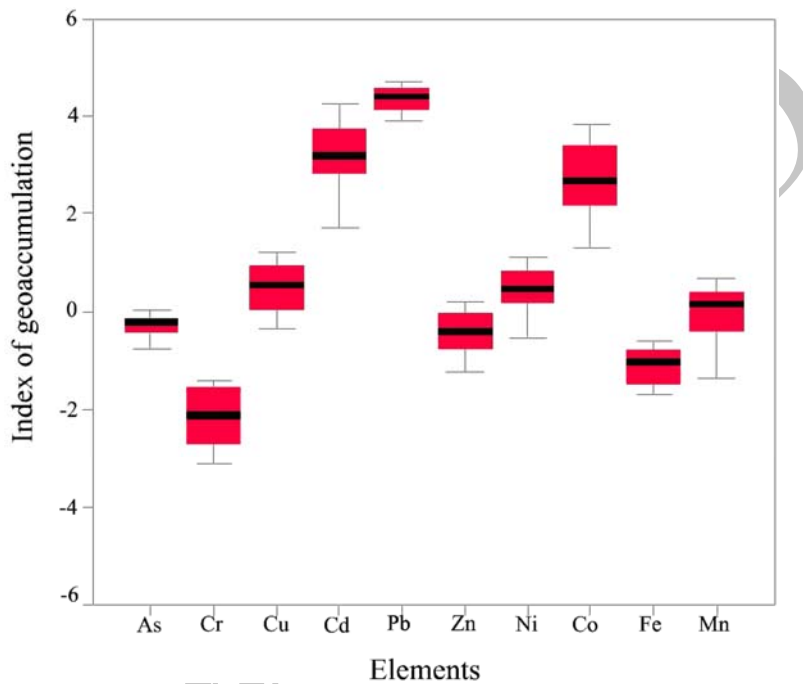


Fig. 5. Box-and-whisker plots of the geoaccumulation index of studied metals in 12 surface sediment samples of Maharlu saline lake

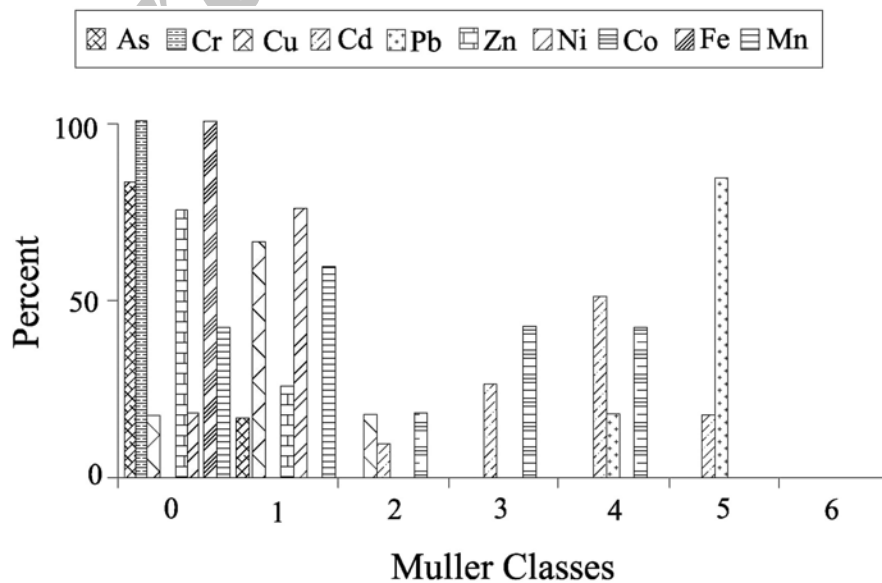


Fig. 6. Percentage of samples in Müller class, using local background sample as reference material

### e) Enrichment factor of heavy metals in surface sediments

Measuring enrichment factor (EF) is an essential part of geochemical studies and is generally used to differentiate between the metals originating from anthropogenic (non-crustal) and geogenic (crustal) sources, and to assess the degree of metal contamination [27, 28, 29]. For enrichment factor values greater than 1 point to sediment contamination,  $0 < EF < 10$  is an indication for natural origin (initial soil or parent rock), while those greater than 10 are considered to be from anthropogenic sources [27].

Figure 7 indicates that enrichment factors for As, Cr, Fe, and Mn vary between 0 and 10, indicating the natural source for these metals in the Maharlu Lake sediments, i.e. they are not affected by anthropogenic influences. For Ni, Zn and Cu, enrichment factor values are  $>10$  north of the lake, and  $<10$  in other areas, whereas the EFs for Cd, Pb, and Co are  $>10$  all over the lake, with the highest values occurring north of the lake. The results indicate that the Khoshk River is the main source of anthropogenic heavy metal loading into the lake. Runoff from nearby soils can add to Cu, Ni, and Zn loading. Sutherland [30] has distinguished five classes of enrichment factors:  $EF < 2$  shows deficiency to low enrichment,  $2 < EF < 5$  shows moderate enrichment,  $5 < EF < 20$  shows significant enrichment,  $20 < EF < 40$  shows very high enrichment, and  $EF > 40$  shows extremely high enrichment. Based on this classification, the Maharlu Lake sediments have deficiency to low enrichment with Fe and Cr, moderate enrichment with Mn, Zn, and As, significant enrichment with Cu and Ni, very high enrichment with Cd and Co, and extremely high enrichment with Pb.

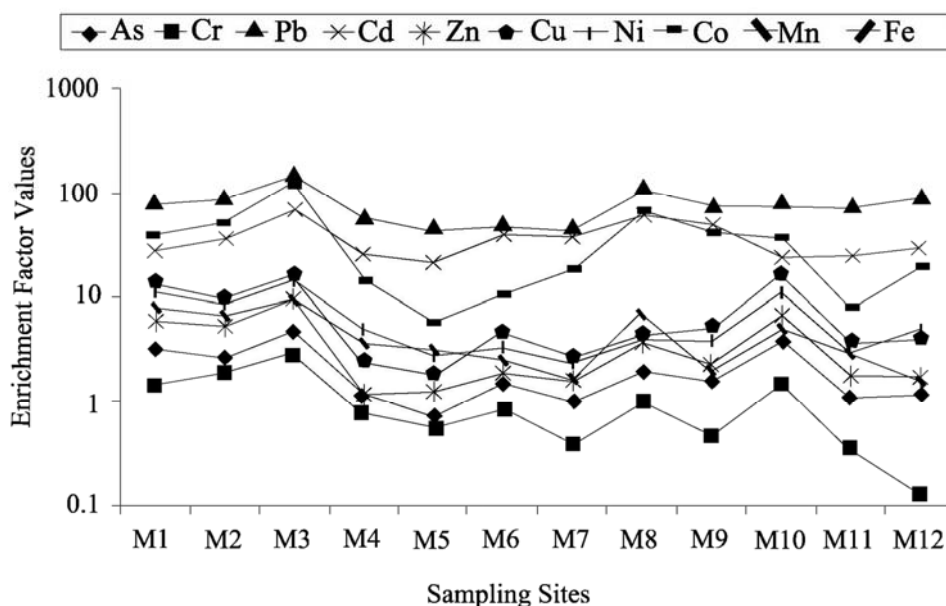


Fig. 7. Enrichment factors for analyzed heavy metals in 12 sampling sites. EF values greater than 10 are indicative of anthropogenic sources

### f) Contamination factor and contamination degree of analyzed metals

Table 4 shows the contamination factor ( $C_f$ ) of each element and also the degree of contamination ( $C_d$ ) for each sampling site. According to the Håkanson classification [17],  $C_f < 1$  points to low contamination factor,  $1 \leq C_f < 3$  points to moderate contamination factor,  $3 \leq C_f < 6$  points to considerable contamination, and  $C_f \geq 6$  points to very high contamination factor. On this basis, the Maharlu Lake has very high  $C_f$  values for Pb, Co, Cd; low  $C_f$  for As, Cr, Fe; moderate  $C_f$  for Zn, Ni, Mn, and Cu. Calculation of the average contamination degree ( $C_d$ ) indicates that the Maharlu Lake is considered to be a lake with a very high contamination degree (Table 4), indicating serious anthropogenic pollution.

Table 4. Contamination factors ( $C_f$ ) and contamination degree ( $C_d$ ) for Maharlu saline Lake

Sampling site	Contamination factor ( $C_f$ )										Contamination degree ( $C_d$ )
	Mn	Fe	Pb	Cd	Zn	Cu	Ni	Co	Cr	As	
M1	2.04	0.77	21.56	3.81	1.46	3.21	2.85	9.73	0.35	0.95	46.73
M2	1.78	0.67	24.09	5.33	1.43	2.46	2.37	14.7	0.5	0.9	54.23
M3	1.66	0.78	26.39	6.60	1.65	2.49	2.79	21.5	0.47	1.07	65.4
M4	2.32	0.66	36.55	7.62	0.73	1.38	3.08	9.26	0.47	0.84	62.91
M5	2.21	0.46	31.31	7.87	0.88	1.17	1.92	3.98	0.41	0.95	51.16
M6	1.60	0.90	29.90	14.48	1.17	2.71	2.04	6.65	0.52	0.91	60.88
M7	1.20	0.66	31.00	14.73	1.16	1.80	1.64	17.34	0.26	0.91	70.7
M8	1.81	0.49	28.32	8.89	0.98	1.07	1.00	20.37	0.24	0.72	63.89
M9	0.9	0.55	34.23	11.68	0.94	2.15	1.70	7.58	0.19	0.77	60.69
M10	1.04	0.77	15.23	2.58	1.33	3.01	2.17	3.75	0.27	0.81	30.96
M11	1.42	0.5	36.24	6.35	0.82	1.62	1.40	7.09	0.16	0.63	56.23
M12	0.57	0.42	32.79	5.84	0.6	1.5	1.66	11.27	0.03	1.53	56.21
Mean values	1.54	0.63	29	8	1.10	2.04	2.05	11.10	0.32	0.91	56.66

The following terminology is adopted to describe the contamination degree for analyzed elements [17].  $C_d < 6$ : Low contamination degree,  $6 \leq C_d < 12$ : Moderate contamination degree;  $12 \leq C_d < 24$ : considerable contamination degree;  $C_d \geq 24$ : very high contamination degree.

#### 4. SUMMARY AND CONCLUSION

The main purpose of this study was to assess the environmental contamination of Maharlu Saline Lake with respect to selected heavy metal concentrations in water and surface sediments. On the basis of the obtained data, the following three main groups of metals can be distinguished:

##### a) Cd, Pb, Co

The surface sediment data show that total concentration of Cd, Co, and Pb is higher than global (average shale, upper continental crust) and local reference materials (the composition of local background sample and soils in the vicinity of the lake). The geochemical calculations indicate that these metals have higher  $EF$ ,  $I_{geo}$ , and  $C_f$  compared with other studied elements. Enrichment factor values for these elements all over the lake are greater than 10; indicating anthropogenic origin of these elements. Results show that Maharlu Lake water is highly polluted with respect to these elements. The results point to the fact that Maharlu Lake is threatened with becoming highly contaminated with Pb, Co, and Cd. However, comparison of the obtained data with SQGs indicates that Cd cannot be considered an ecotoxicological risk for the aquatic biota, whereas Pb must be considered a serious threat for the lake ecosystem.

##### b) Ni, Cu, Zn

The total concentrations of Zn, Cu, and Ni in sediments, respectively, are comparable with global and local reference materials. Geochemical calculations indicate that this group of elements has less significance than the first group. The enrichment factors of Ni, Cu, and Zn are higher than 10 only north of the lake, and their concentration in the lake water is high. These results confirm that Ni, Cu, and Zn pollution in the Maharlu Lake can be attributed to discharge of untreated industrial and urban wastewaters from the Khoshk River which discharges north of the lake. In the context of ecotoxicological impact, Ni is dangerous for aquatic life, whereas Zn poses no risk.

##### c) As, Cr, Fe, Mn

The concentration of Fe, As and Cr in lake sediments is lower than global reference materials; however, their concentration in soils is higher than those in lake sediments. Geochemical calculations indicate that these elements have the lowest significance for lake contamination. The concentrations of As

and Cr in the lake water were below detection limits, however, they have an ecotoxicological risk for aquatic life. These results indicate that arsenic and Cr mainly come from natural sources. Soil run off can contribute to the loading of this group of elements into the lake.

Results of this study provide baseline data which can be used by authorities for environmental management. It can be concluded that the input of various wastewaters into the Maharlu Lake is responsible for the intense pollution of the water and sediments, and must be regarded as a major concern. In order to protect the lake from further contamination, the following approaches are suggested:

1. Designing a monitoring network to trigger preventive actions
2. Reducing the anthropogenic discharges into the lake. For this purpose, environmental remediation and treatment of wastewaters introduced into the Khoshk River is essential.
3. Preventing direct input of agricultural runoff
4. Minimizing metal remobilization impacts by improving the quality of water through sediment dredging.

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## REFERENCES

1. Oyewale, A. O. & Musa, I. (2006). Pollution assessment of the lower basin of Lakes Kainji/Jebba, Nigeria: heavy metal status of the waters, sediments and fishes. *Environ. Geochem. Health*, 28, 273-281.
2. Sin, S. N., Chua, H., Lo, W. & Ng, L. M. (2001). Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. *Environ. Int*, 26, 297-301.
3. Kische, M. A. & Machwa, J. F. (2003). Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. *Environ Int*, 28, 619-625.
4. Ahmed, F., Bibi, H. M., Monsur, H. M. & Ishiga, H. (2005). Present environment and historic changes from the record of lake sediments, Dhaka City, Bangladesh. *Environ. Geol*, 48, 25-36.
5. Markus, J. & McBratney, A. B. (2001). A review of the contamination of soil with lead II. Spatial distribution and risk assessment of soil lead. *Environ. Int*, 27, 399-411.
6. Nadal, M., Schuhmacher, M. & Domingo, J. L. (2004). Metal pollution of soils and vegetation in an area with petrochemical industry. *Sci. Total Environ*, 321, 59-69.
7. Ochieng, E. Z., Lalah, J. O. & Wandiga, S. O. (2007). Analysis of heavy metals in water and surface sediment in five Rift Valley Lakes in Kenya for assessment of recent increase in anthropogenic activities. *Bull. Environ. Contam. Toxicol*, 79, 570-576.
8. An, Y. J. (2006). Assessment of comparative toxicities of lead and copper using plant assay. *Chemosphere*, 62, 1359-1365.
9. Wu, Y., Hou, X., Cheng, X., Yao, S., Xia, W. & Wang, S. (2007). Combining geochemical and statistical methods to distinguish anthropogenic source of metals in lacustrine sediment: a case study in Dongjiu Lake, Taihu Lake catchment, China. *Environ. Geol*, 52, 1467-1474.
10. Lee, S., Moon, J. I. W. & Moon, H. I. S. (2003). Heavy metals in the bed and suspended sediments of Anyang River, Korea: Implications for water quality. *Environ. Geochem. Health*, 25, 433-452.
11. Qishlaqi, A., Moore, F. & Forghani, G. (2008). Impact of untreated wastewater irrigation on soils and crops in Shiraz suburban area, SW Iran. *Environ. Monit. Assess*, 141, 257-273.
12. Fukue, M., Yanai, M., Sato, Y., Fujikawa, T., Furukawa, Y. & Tani, S. (2006). Background values for evaluation of heavy metal contamination in sediments. *J. Hazard. Mater*, 136, 111-119.

13. Duquesne, S., Newton, L. C., Giusti, L., Marriott, S. B., Stark, A. J. & Bird, D. J. (2006). Evidence for declining levels of heavy metals in the Severn Estuary and Bristol Channel, U.K., and their spatial distribution in sediments. *Environ. Pollut*, 143, 187-196.
14. Farkas, A., Erratico, C. & Vigano, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68, 761-768.
15. Jeffery, P. G. & Hutchinson, P. (1983). *Chemical methods of rock analysis*. Third edition, Pergamon. P. 379.
16. Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geol. Jour*, 2, 109-118.
17. Håkanson, L. (1980). An ecological risk index for aquatic pollution control—a sedimentological approach. *Water Res*, 14, 975-1001.
18. Turekian, K. K. & Wedepohl, K. H. (1961). Distribution of elements in some major units of the earth's crust. *Geol. Soc. of American Bull*, 72, 175-192
19. Taylor, S. R. & McLennan, S. M. (1985). *The continental crust: its composition and evolution*. London, Blackwell.
20. Dekov, V. M., Araujo, F., Van Grieken, R. & Subramanian, V. (1998). Chemical composition of sediments and suspended matter from the Cauvery and Brahmaputra rivers (India). *Sci. Total Environ*, 212, 89-105.
21. Roussiez, V., Ludwig, W., Monaco, A., Probst, J. L., Bouloubassi, I., Roselyne, B. & Saragoni, G. (2006). Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW Mediterranean Sea): a multi-tracer approach. *Cont. Shelf Res*, 26, 1843-1857.
22. McDonald, D. D., Ingersoll, C. G. & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol*, 39, 20-31.
23. Hsu, M. J., Selvaraj, K. & Agoramorthy, G. (2006). Taiwan's industrial heavy metal pollution threatens terrestrial biota. *Environ. Pollut*, 143, 327-334.
24. Samecka-Cymerman, A. & Kempers, A. J. (2001). Concentrations of heavy metals and plant nutrients in water, sediments, and aquatic macrophytes of anthropogenic lakes (former open cut brown coal mines) differing in stage of acidification. *Sci. total. environ*, 281, 87-98
25. Markert, B. (1994). Inorganic chemical fingerprinting of the environment; reference freshwater, a useful tool. *Fresenius J. Anal. Chem*, 349, 697-702.
26. Health Canada (2003). Federal-Provincial Advisory Committee on Environmental and Occupational Health, Guidelines for Canadian Drinking Water Quality.
27. Selvaraj, K., Moha, V. R. & Szefer, P. (2004). Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. *Mar. Pollut. Bull*, 49, 174-185.
28. Olivares-Rieumont, S., Rosa, D. D. L, Lima, L., Graham, D. W., Alessandro, K. D., Borroto, J., Martinez, F. & Sanchez, J. (2005). Assessment of heavy metal levels in Almendared River sediments-Havana City, Cuba. *Water Res*, 39, 3945-3953.
29. Yongming, H., Peixuan, D., Junji, C. & Posmentier, E. S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *Sci. Total Environ*, 355, 176-186.
30. Sutherland, R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol*, 39, 611-627.

## ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER AND SURFACE SEDIMENTS OF THE MAHARLU SALINE LAKE, SW IRAN\*

F. MOORE<sup>1\*\*</sup>, G. FORGHANI<sup>2</sup> AND A. QISHLAQI<sup>3</sup>

Department of Earth Sciences, Faculty of Sciences, Shiraz University, Shiraz, I. R. Iran

<sup>1</sup>Moore@geology.susc.ac.ir

<sup>2</sup>gforghani@gmail.com

<sup>3</sup>Qishlaqi@shirazu.ac.ir

### ارزیابی آلودگی فلز سنگین آب و رسوبات سطحی دریاچه شور مهارلو، جنوب غرب ایران

ف. مَر، گ. فرقانی و ا. قشلاقی

بخش علوم زمین، دانشکده علوم، دانشگاه شیراز، شیراز، جمهوری اسلامی ایران

**چکیده:** به منظور ارزیابی آلودگی زیست محیطی دریاچه مهارلو واقع در جنوب غرب ایران، غلظت کل عناصر آرسنیک، کرم، کبالت، مس، کادمیم، سرب، روی، نیکل، آهن، و منگنز در رسوبات سطحی و آب دریاچه اندازه گیری شد. غلظت آرسنیک و کرم در نمونه های آب زیر حد آشکارسازی دستگاه بود، در حالی که میانگین غلظت دیگر فلزات حل شده به صورت زیر می باشد:  $0.28 \text{ mg/l}$  مس،  $0.28 \text{ mg/l}$  کادمیم،  $5.17 \text{ mg/l}$  سرب،  $0.37 \text{ mg/l}$  روی،  $2.36 \text{ mg/l}$  نیکل،  $2.88 \text{ mg/l}$  کبالت،  $10.4 \text{ mg/l}$  آهن، و  $1.5 \text{ mg/l}$  منگنز. بکارگیری رویکردهای مختلف ارزیابی کیفیت آب و رسوب نشان داد که فلزات را می توان به سه گروه مختلف تقسیم بندی کرد: الف) کبالت، سرب، و کادمیم. در مقایسه با دیگر عناصر مورد مطالعه، این فلزات دارای بالاترین ضرایب غنی شدگی، ضرایب زمین انباشت، و ضرایب آلودگی هستند؛ ب) مس، روی، و نیکل. متوسط ضریب غنی شدگی این عناصر بین ۱ تا ۱۰؛ متوسط ضرایب زمین انباشت آنها کمتر از ۱، و میانگین ضریب آلودگی آنها به ترتیب ۲، ۱/۱، و ۲ می باشد. ج) کرم، آرسنیک، آهن و منگنز. این عناصر پایینترین ضرایب غنی شدگی، ضرایب زمین انباشت، و ضرایب آلودگی را نشان می دهند؛ بنابراین دریاچه مهارلو نسبت به این عناصر آلوده نیست. نتایج به دست آمده نشان می دهد که رسوبات دریاچه مهارلو درجه آلودگی بالا را نشان می دهند. در مقایسه با مقادیر استاندارد کیفیت رسوب، نیکل و سرب بیشترین تهدید زیست محیطی برای ارگانیزمهای آبگین دریاچه محسوب می شوند.