CHARACTERIZATION OF METAL POLLUTION IN SURFACE SEDIMENTS ALONG THE NORTHEASTERN COAST OF LIBYA

OMAR, W. A.[1*] – BUSAADIA, M. A.[2] – SALEH, Y. S.[3] – ALMALKI, A. S. A.[4] – MARIE, M-A. S.[5]

[1] *Department of Biology, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia*

[2] *Department of Environmental Health, Faculty of Public Health, Benghazi University, Benghazi, Libya*

[3] *Department of Biology, Faculty of Science, Taiz University, Taiz, Yemen*

[4] *Department of Chemistry, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia*

[5] *Department of Zoology, Faculty of Science, Cairo University, Cairo, Egypt*

**Corresponding author*
e-mail: w.omar@tu.edu.sa; phone: +966-537-850-960
ORCID https://orcid.org/0000-0002-4933-5499

(Received 28th Sep 2021; accepted 22nd Dec 2021)

Abstract. The present investigation aimed to assess metal pollution status (Fe, Al, Cu, Zn, Mn, Cd and Pb) in sediments of four cities along the northeastern coast of Libya. The mean metal concentrations in sediment samples from highest to lowest showed the following order Al > Fe > Mn > Zn > Cu > Pb > Cd. All metal concentrations were lower than their background values except for Cd at sites 1, 2 and 3. Sediment quality guidelines showed that biological hazardous effects are related to 25% of Cd samples while other studied metals are biologically safe. The overall evaluation indicates moderate to severe pollution status with Cd along sites 1 and 3 while other metals showed marginal or safe limits. Metal pollution status along the coastline of major cities proved indisputably to be due to anthropogenic activities. The geoaccumulation index (I_{geo}) showed efficient indication of individual metals while the potential ecological risk index (RI) could clearly discriminate the risks posed by metal mixtures.
Keywords: *Mediterranean Sea, sediment quality, anthropogenic activities, ecological risks*

Introduction

The Mediterranean coastline of Libya extends for about 1950 km starting from the western borders with Tunisia to the eastern borders with Egypt. The Libyan coast and its lagoons play an important role in the biodiversity and productivity of the Mediterranean marine life as it is characterized by gigantic beds of marine plants serving as important feeding and nursery grounds for different marine species. Thus it is considered one of the most productive commercial fisheries along North Africa (Haddoud and Rawag, 2007). Rapid industrialization and uncontrolled urbanization around many Libyan cities and coastal areas have brought alarming levels of metal contamination to the aquatic environment as metals have high enrichment factors and slow removal rates (Soliman et al., 2015). Metals constitute a core group of aquatic pollutants and have a particular significance in ecotoxicology due to their high persistence as well as non-biodegradable and bio-accumulative properties (Paudel et al., 2016). The elevated metal levels in aquatic ecosystems raises worldwide environmental and health concerns (Rakib et al., 2021).

DOI: http://dx.doi.org/10.15666/aeer/2002_13991412

Pollutants related to anthropogenic activities have various sources such as mining, industry, urbanization, agriculture and many other every-day activities. Metals released from mining and industrial processes are among the major contaminants of concern in marine environments, where they accumulate in the water, sediments and marine organisms. Sources of pollution in aquatic ecosystems are mostly land-based but in some cases, the pollutants originate or remobilize in the aquatic environment itself (Tornero and Hanke, 2016). Integrated management strategies to protect aquatic ecosystems include evaluating metal pollution of sediments as well as differentiating the influence of natural and/or anthropogenic sources (Yu et al., 2008).

Procedures of sediment pollution assessment using calculated indices such as contamination factor (CF), enrichment factor (EF), modified contamination degree (mC_d), pollution load index (PLI) and geoaccumulation index (I_{geo}) are widely applied to evaluate metal pollution status and enrichment in sediments (Wang et al., 2014; Omar et al., 2016; Saleh, 2021). These indices are considered as sensitive indicators of the influence of different anthropogenic activities on aquatic ecosystems (Omar et al., 2016).

The present work aims to characterize metal pollutants in sediments of four coastal sites with different levels of anthropogenic activities along the northeastern coast of Libya.

Materials and Methods

The study sites

The Mediterranean Sea coast of Libya is closely associated with the major geological features of the African continent. The hydrological conditions of the region are dominated by three layers of water masses, which are the surface layer, the intermediate layer and the deep layer also it is characterized by lack of natural freshwater inputs (Al-Hassan, 1999). The Libyan coastline has four important lagoons, which are Farwa (at the northwestern coast), Ain Zayana (Benghazi city), Ain Gazala (Tobruk city) and Al-Burdy lagoons (Kerambrun, 1986). Three of these lagoons are located in the northeastern coast of Libya and were investigated in the present work.

Site 1: located at Ain Zayana lagoon, Benghazi city, with GPS coordinates of 32° 14' 59.98" N, 20° 4' 47.72" E. Benghazi is the second largest Libyan city after Tripoli. The city is characterized by its port on the Mediterranean Sea with various urban and industrial activities.

Site 2: located at Susah city with GPS coordinates of 32° 55' 6.49" N, 21° 57' 26.23" E. The area is characterized by its shallow waters suitable for fishing activities which are uncontrolled or illegal in most cases.

Site 3: located at Ain Ghazala lagoon, Tobruk city, with GPS coordinates of 32° 3' 51.37" N, 24° 1' 14.00" E. The city is well known by the shipping and shipment activities associated with oil pollution.

Site 4 (Reference site): located at Al-Burdy lagoon, Al-Burdy city, with GPS coordinates of 31° 45' 38.32" N, 25° 6' 11.20" E. The city is characterized by minor urban activities which are mostly eco-friendly, thus this site is considered as a reference site in the present study.

The four sites cover a distance of about 500 km along the Libyan Mediterranean coast (*Fig. 1*).

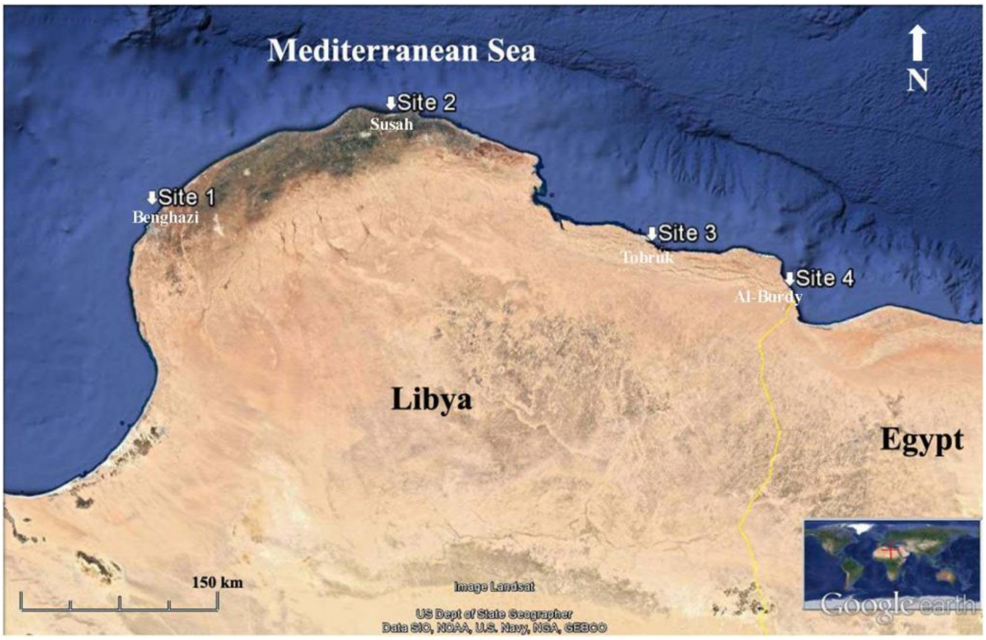

Figure 1. *Map of the study sites*

Sediment sampling

Duplicates of eight surface sediment samples, up to 10 cm in depth, were collected using sampling dredge from four localities in a radius of 1 km^2 around the reported GPS coordinates of the studied during summer season 2019. The samples were immediately stored at 4ºC for further analyses (Cabrera et al., 1992).

Metal concentrations in sediment samples

Sediment samples were dried at 105ºC for 12 hours then burned in a muffle furnace at 550ºC for 16 hours. Samples were then acid digested and diluted with de-ionized water to known volume using the dry ashing procedure proposed by Issac and Kerber (1971) and Hseu (2004). Metal concentrations (Fe, Al, Cu, Zn, Mn, Cd and Pb) were determined using flame atomic absorption spectrophotometer (Thermo Scientific ICE 3300, UK) provided with double beam and deuterium background corrector according to APHA (2005).

Quality assurance and quality control (QA/QC) procedures

Analytical blanks were run in the same way as the samples, and metal concentrations were determined using standard solutions prepared in the same acid matrix. All used reagents were of analytical grade (Merck Co.). Standards for instrument calibration were prepared on the basis of mono-element certified reference solution (Merck Co.). Standard reference material (SRM 2702) was used to validate extraction procedures. All analyses were carried out in duplicates and the metal recoveries ranged from 92 to 107% for all measured samples.

Risk assessment of sediment pollution

Sediment quality guidelines (SQGs)

The detected metal concentrations were compared to the corresponding quality guidelines. Two sets of SQGs proposed by the U.S. National Oceanic and Atmospheric Administration (NOAA) and Canadian guidelines developed for marine sediment (MacDonald et al., 2000) were applied in the present study: (1) the threshold effect level (TEL)/probable effect level (PEL) values; and (2) the effect range low (ERL)/effect range-median (ERM) (Long et al., 1995; MacDonald et al., 2000).

Contamination factor (CF)

It was calculated using the following equation (*Eq. 1*) (Hakanson, 1980).

$$\mathrm{CF_i} = Cm_i \,/\, Cb_i \qquad \text{(Eq.1)}$$

where Cm_i is the mean concentration of metal i in sediment sample and Cb_i is the background value, also called shale value or crustal value, of that metal. The average background values of the studied metals as indicated by Turekian and Wedepohl (1961) are 46000, 80000, 45, 95, 850, 0.3 and 20 mg/kg dry wt. for Fe, Al, Cu, Zn, Mn, Cd and Pb, respectively.

Enrichment factor (EF)

Calculation of EF involves normalization of the detected metal with respect to a reference element such as Al, Fe and Mn (Karbassi et al., 2008). Al was used as a normalizer as it exists in sediments at a respective high level and it is rich in the Earth's crust assuming that it is free from anthropogenic impact. EF values for each metal in sediment were calculated as follows (*Eq. 2*) (Buat-Menard and Chesselet, 1979).

$$\mathrm{EF} = (Cm_i/C_{\mathrm{Al}})_{sample} \,/\, (Cm_i/C_{Al})_{background} \qquad \text{(Eq.2)}$$

where $(Cm_i/C_{\mathrm{Al}})_{sample}$ is the ratio of concentration of metal i to that of Al in each sampling site and $(Cm_i/C_{Al})_{background}$ is the same ratio of the background concentrations reported by Turekian and Wedepohl (1961).

Modified contamination degree (mC_d)

It was applied to estimate the overall contamination degree at a particular site based on the following equation (*Eq. 3*) (Abrahim and Parker, 2008).

$$\mathrm{mC_d} = \sum_{\mathrm{i=1}}^{\mathrm{n}} CF_i \,/\, n \qquad \text{(Eq.3)}$$

where n is the number of the studied metals.

Pollution load index (PLI)

The PLI was calculated using the following equation (*Eq. 4*) (Tomlinson et al., 1980).

$$\mathrm{PLI} = \left(\prod_{i=1}^{n} CF_i\right)^{1/n} \qquad \text{(Eq.4)}$$

DOI: http://dx.doi.org/10.15666/aeer/2002_13991412

PLI < 1 indicates safe limits, whereas PLI ≥ 1 indicates progressive pollution (Tomlinson et al., 1980).

Mean effect range-median quotient (M-ERM-Q)

The mean ERM quotient (M-ERM-Q) was calculated according to the following equation (*Eq. 5*) (Long et al., 2000).

$$\text{M-ERM-Q} = \frac{\sum_{i=1}^{n} Cmi\ /\ ERM}{n} \qquad \text{(Eq.5)}$$

where *ERM* is the effect range median of the metal. The *ERM* values of Cu, Zn, Cd and Pb are 270, 410, 9.6 and 218, respectively (Long et al., 1995).

Potential ecological risk

The potential ecological risk factor (Er_i) and the potential ecological risk index (RI) were calculated according to Hakanson (1980) as (*Eq. 6* and *Eq. 7*, respectively)

$$Er_i = Tr_i \times CF_i \qquad \text{(Eq.6)}$$

$$\text{RI} = \sum_{i=1}^{n} Er_i \qquad \text{(Eq.7)}$$

where Tr_i is the toxic response factor of metal *i*. The toxic response factors of Cu, Zn, Cd and Pb are 5, 1, 30 and 5, respectively (Hakanson, 1980) and that of Mn is 1 (Xu et al., 2008).

Geoaccumulation index (I_{geo})

A common approach to estimate the enrichment of metal concentrations above the background or baseline concentrations is to calculate the geoaccumulation index (I_{geo}). The I_{geo} values were calculated for the studied metals as indicated by Müller (1969) as (*Eq. 8*):

$$I_{geo} = Log_2\,[Cm_i\ /\ (1.5 \times Cb_i)] \qquad \text{(Eq.8)}$$

where, the 1.5 factor is the background matrix correction factor. Lu et al. (2009) defined the background matrix correction factor as a constant introduced to minimize the effect of possible variations in the background values, which may be attributed to lithologic variations in sediments.

Quality criteria of SQGs and all studied ecological risk assessment indices are illustrated in *Table 1*.

Statistical analyses

The results are expressed as mean ±S.E. Data were statistically analyzed using one-way analysis of variance (ANOVA) and Duncan’s multiple range test to determine difference in means as indicated by different case letters in the descending order A, B, C and D at $P<0.05$ using SAS (Statistical Analysis System) version 9.1 (SAS, 2006).

Table 1. *Quality criteria of SQGs and ecological risk assessment indices*

Index	Classification	Description	Reference
TEL and PEL guidelines	< TEL	Not associated with hazardous biological effects	MacDonald et al. (2000)
	≥ TEL < PEL	May occasionally be associated with hazardous biological effects	
	≥ PEL	Frequently associated with hazardous biological effects	
ERL and ERM guidelines	< ERL	Minimal effects range	Long et al. (1995)
	≥ ERL < ERM	Effects would occasionally occur	
	≥ ERM	Effects would frequently occur	
Contamination factor (CF)	< 1	Low contamination	Hakanson (1980)
	1 - 3	Moderate contamination	
	3 - 6	Considerable contamination	
	> 6	Very high contamination	
Enrichment factor (EF)	< 1	No enrichment	Birch and Olmos (2008)
	1-3	Minor enrichment	
	3-5	Moderate enrichment	
	5-10	Moderately severe enrichment	
	10-25	Severe enrichment	
	≥ 25	Extremely severe enrichment	
Modified contamination degree (mC_d)	< 1.5	Nil to very low degree of contamination	Abrahim and Parker (2008)
	1.5 - 2	Low degree of contamination	
	2 - 4	Moderate degree of contamination	
	4 - 8	High degree of contamination	
	8 - 16	Very high degree of contamination	
	16 - 32	Extremely high degree of contamination	
	> 32	Ultra-high degree of contamination	
Mean effect range-median quotient (M-ERM-Q)	< 0.1	9% probability of toxicity	Long et al. (2000)
	0.11 - 0.5	21% probability of toxicity	
	0.51 - 1.5	49% probability of toxicity	
	> 1.5	76% probability of toxicity	
Potential ecological risk factor (*Eri*)	< 40	Low risk	Hakanson (1980)
	40 - 80	Moderate risk	
	80 - 160	Considerable risk	
	160 - 320	High risk	
	> 320	Very high risk	
Potential ecological risk index (RI)	< 50	Low risk	Hakanson (1980)
	50 - 100	Moderate risk	
	100 - 200	Considerable risk	
	> 200	Very high risk	
Geoaccumulation index (I_{geo})	< 0	Unpolluted	Müller (1969)
	0 - 1	Unpolluted to moderately polluted	
	1 - 2	Moderately polluted	
	2 - 3	Moderately to heavily polluted	
	3 - 4	Heavily polluted	
	4 - 5	Heavily to extremely polluted	
	> 5	Extremely polluted	

Results and Discussion

Metal concentrations

Metal concentrations along the studied sites showed the order Al > Fe > Mn > Zn > Cu > Pb > Cd (*Table 2*). All detected mean values were less than their corresponding background values except for Cd in sites 1, 2 and 3. The highest values of Cd and Zn were recorded significantly in site 1 followed by site 3. Meanwhile the highest values of Cu and Pb were recorded significantly in both sites 1 and 3. The lowest values of Cd, Zn, Cu and Pb were recorded in site 4 (the reference site). Omar et al. (2016) reported that Cd, Zn, Cu and Pb are the main metal pollutants in sediments arising from anthropogenic inputs. Meanwhile manganese, iron and aluminium are common natural components of the Earth's continental crust (WHO, 2017), thus have no significance as sediment pollutants unless their current concentrations exceed their corresponding background concentrations. However, their nanoparticles occurring in anthropogenic effluents, such as iron based nanoparticles, have high efficiencies to adsorb other metals due to their large surface areas and the linked particles mostly settle on surface sediments (Alhadhrami et al., 2019). Yu et al. (2008) mentioned that marine sediments act as the ultimate destination of metal pollutants into the aquatic ecosystems.

Table 2. *Metal concentrations (mg/kg dry wt.; mean ±SE) in sediment samples and sediment quality guidelines (SQGs)*

		Fe	**Al**	**Cu**	**Zn**	**Mn**	**Cd**	**Pb**
Sampling sites	Site 1	424.80 $\pm 8.85^{AB}$	365.0 $\pm 20.18^{C}$	4.32 $\pm 0.14^{A}$	7.87 $\pm 0.32^{A}$	34.14 $\pm 1.99^{C}$	0.83 $\pm 0.11^{A}$	1.10 $\pm 0.19^{A}$
	Site 2	413.60 $\pm 95.40^{B}$	560.90 $\pm 13.78^{A}$	3.48 $\pm 0.12^{B}$	4.90 $\pm 1.33^{C}$	63.23 $\pm 1.65^{B}$	0.43 $\pm 0.02^{C}$	0.61 $\pm 0.13^{B}$
	Site 3	481.70 $\pm 38.01^{A}$	448.80 $\pm 24.98^{B}$	4.20 $\pm 0.54^{A}$	6.29 $\pm 0.36^{B}$	32.56 $\pm 1.44^{C}$	0.66 $\pm 0.03^{B}$	1.14 $\pm 0.48^{A}$
	Site 4	477.0 $\pm 54.86^{A}$	545.20 $\pm 25.36^{A}$	3.43 $\pm 0.13^{B}$	4.03 $\pm 0.14^{D}$	94.18 $\pm 2.28^{A}$	0.27 $\pm 0.06^{D}$	0.16 $\pm 0.01^{C}$
TEL*				19	124		0.7	30
PEL*				108	271		24	112
ERL**				34	150		1.2	46.7
ERM**				270	410		9.6	218
Percentage of TEL and PEL guidelines								
< TEL				100	100		75	100
≥ TEL < PEL				0	0		25	0
≥ PEL				0	0		0	0
Percentage of ERL and ERM guidelines								
< ERL				100	100		100	100
≥ ERL < ERM				0	0		0	0
≥ ERM				0	0		0	0

Statistical significant differences ($P<0.05$) are shown with different capital letters along the studied sites for each metal. TEL: Threshold effect level; PEL: Probable effect level; ERL: Effect range-low; ERM: Effect range-median, * MacDonald et al. (2000), ** Long et al. (1995)

The detected elevated levels of Cu, Zn, Cd, and Pb in site 1 and site 3, are directly associated with different anthropogenic activities including illegal fishing prevailing at these areas and untreated sewage discharge. Metwally and Fouad (2008) illustrated that the concentrations of Cu, Pb, Zn, Cd and Hg along Khomse coast, Libya, significantly increased in comparison to their concentrations 17 years ago, except for Cd. They also indicated that untreated domestic wastewater as well as agricultural and industrial wastes are discharged directly through many drainages and outfalls along this coastal area.

The detected high concentrations of Al in all studied sites is in agreement with Abdel-Ghani (2015) who detected elevated levels of Al among other studied metals in samples collected from Marsa Matrouh City at the northwestern Mediterranean coast of Egypt. Sadauskas-Henrique et al. (2011) stated that sewage effluents contain high levels of Fe, Cd, Cu, Zn, Mn and Pb.

Consequently, assessment of metal pollutants in marine sediments of sites nearby populated areas is useful to investigate anthropogenic impacts on ecosystems and to indicate risks posed by waste discharges (Yi et al., 2011; Saleh, 2021). In addition, these persistent pollutants may remain for a long time in the ecosystem even after cutting-off direct inputs (Ali and Abdel-Satar, 2005).

Risk assessment of sediment pollution

SQGs indicate the possibility that a sediment associated toxicant may cause hazardous biological effects as well as impairment of aquatic organisms and the entire aquatic ecosystem (MacDonald et al., 2000). TEL and PEL guidelines showed lower concentrations of Cu, Zn and Pb than their TEL values indicating no association with hazardous biological effects. Meanwhile, 75% of Cd samples were lower than its TEL value while 25% of samples lied between its TEL and PEL values and may occasionally be associated with hazardous biological effects. 100% of Cu, Zn, Cd and Pb samples were lower than their ERL values illustrating a minimal effects range (*Tables 1 and 2*). Several risk indices including SQGs, CF, EF, Er_i and I_{geo} are useful in assessing adverse effects of individual metals but do not consider the cumulative effect of several metals in mixture as usually encountered in most environmental conditions. The cumulative effect of a metal mixture is assessed by mC_d, PLI, M-ERM-Q and RI (Saleh, 2021).

Values of CF, EF, mC_d, PLI and M-ERM-Q of metals are illustrated in *Table 3*.

Table 3. *Contamination factor (CF), enrichment factor (EF), modified contamination degree (mC_d), pollution load index (PLI) and mean effect range-median quotient (M-ERM-Q) of metals in sediment samples*

	Site 1		**Site 2**		**Site 3**		**Site 4**	
	CF	**EF**	**CF**	**EF**	**CF**	**EF**	**CF**	**EF**
Fe	0.009	1.98	0.009	1.28	0.010	1.86	0.010	1.53
Al	0.005	-	0.007	-	0.006	-	0.007	-
Cu	0.096	19.70	0.077	10.30	0.093	15.60	0.076	10.50
Zn	0.083	21.50	0.052	8.70	0.066	14.0	0.042	7.40
Mn	0.040	9.40	0.074	11.30	0.038	7.30	0.111	17.30
Cd	2.760	566.40	1.440	192.80	2.210	369.10	0.890	122.40
Pb	0.053	9.60	0.030	3.60	0.057	8.40	0.008	1.0
mC_d	0.43		0.24		0.35		0.16	
PLI	0.06		0.05		0.06		0.04	
M-ERM-Q	0.031		0.026		0.027		0.027	

The calculated CF values (*Table 3*) and their related guidelines (Hakanson, 1980) showed that all studied sites had low metal contamination levels (CF < 1) except for cadmium in sites 1, 2 and 3 that showed moderate contamination levels ($1 \leq$ CF < 3).

Based on EF values (*Table 3*) and their quality criteria (Birch and Olmos, 2008), Fe showed minor enrichment along all sites ($1 \leq$ EF < 3). Cu showed severe enrichment ($10 \leq$ EF < 25) along all sites. Zn showed severe enrichment ($10 \leq$ EF < 25) in site 1 and site 3 while it showed moderate severe enrichment ($5 \leq$ EF < 10) in site 2 and site 4. Mn showed severe enrichment ($10 \leq$ EF < 25) in site 2 and site 4 while it showed moderate severe enrichment ($5 \leq$ EF < 10) in site 1 and site 3. Cd showed extreme severe enrichment (EF ≥ 25) along all sites. Pb showed moderate severe enrichment in site 1 and site 3, moderate enrichment in site 2 and minor enrichment in site 4. EF calculations for Al were not conducted due to its usage as a normalizer (reference element) in EF calculations of other metals.

According to Ergin et al. (1991), EF value < 1.5 indicate a natural source of metal. Meanwhile, EF value ≥ 1.5 indicate anthropogenic sources. All metals' EF values of the present study correspond to anthropogenic activities except for Fe in site 2 and Pb in site 4.

All detected mC_d values (*Table 3*) are less than 1.5 indicating nil to very low contamination degree (Abrahim and Parker, 2008). Also PLI values (*Table 3*) were lower than 1 indicating that sediment samples collected from all sites were in safe limits (Tomlinson et al., 1980). The mC_d and PLI were applied to determine the overall metal accumulation at the studied sites. Meanwhile, the M-ERM-Q was used to evaluate the potential biological effect of metals in mixture. All detected M-ERM-Q values (*Table 3*) were lower than 0.1 showing 9% probability of toxicity (Long et al., 2000).

The Er_i and RI are illustrated in *Table 4*. Values of Er_i of Cd in site 2 and site 3 showed moderate risk ($40 \leq Er_i < 80$) while in site 1 it showed considerable risk ($80 \leq Er_i < 160$). All other Er_i of metals along the studied sites showed low risk ($Er_i < 40$) (Hakanson, 1980). Meanwhile, RI values showed low risk in site 2 and site 4 (RI < 50) while it showed moderate risk in site 1 and site 3 ($50 \leq$ RI < 100) (Hakanson, 1980).

Table 4. *The potential ecological risk factor (Eri) and the potential ecological risk index (RI) of metals in sediment samples*

	Er_i					**RI**
	Cu	**Zn**	**Mn**	**Cd**	**Pb**	
Site 1	0.48	0.08	0.04	82.8	0.27	83.67
Site 2	0.39	0.05	0.07	43.2	0.15	43.86
Site 3	0.47	0.07	0.04	66.3	0.29	67.17
Site 4	0.38	0.04	0.11	26.7	0.04	27.27

The I_{geo} values of Cd confirm the present findings where site 1 and site 3 were unpolluted to moderately polluted with Cd ($0 \leq I_{geo} < 1$) while site 2 and site 4 were unpolluted with Cd ($I_{geo} < 0$). Sediment samples of all other sites were unpolluted with Fe, Al, Cu, Zn, Mn and Pb ($I_{geo} < 0$) (*Fig. 2 and Table 1*). The I_{geo} indicates metal enrichment in sediments in relation to background concentrations (Zhang et al., 2009). However, it is not analogous to other pollution indices because its calculation involves a logarithmic function and a correction factor (Zahra et al., 2014).

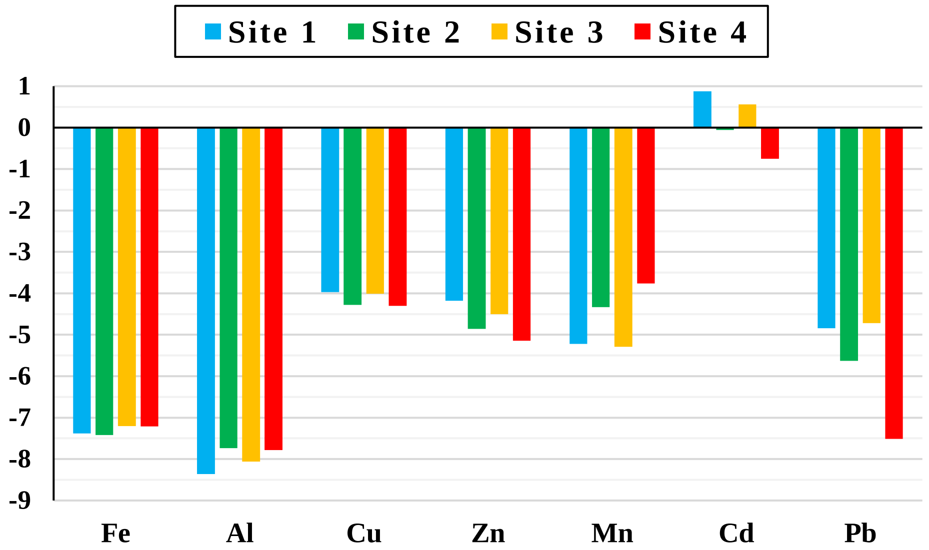

Figure 2. *Geoaccumulation index (I_{geo}) of metals in sediment samples*

The formerly discussed risk assessment indices have been widely used to evaluate the contamination degree and sediment enrichment due to different anthropogenic inputs (Wang et al., 2014; Omar et al., 2016; Saleh, 2021). The background values used to interpret geochemical data have a specific importance. The continental crustal values are usually used as reference baselines. Alternatively, the obtained data are compared to previously reported local or regional data (Birch, 2017). Due to lack or variations of reference data of metal concentrations along the study area, the background values reported by Turekian and Wedepohl (1961) were utilized.

The present findings confirm cadmium pollution condition in site 1 and site 3. These results coincide with Hamouda and Wilson (1989) who confirmed elevated levels of metals (Cu, Ni, Mn, Zn and Cd) in surface sediments of Benghazi Bay, Libya, especially Cd and Cu indicating hazardous anthropogenic activities. Moreover, Hasan and Ul Islam (2010) reported significant increase in metal concentrations (Fe, Mn, Zn, Cu, Cd, Co, Pb, Ni and Cr) in sites polluted with domestic, agricultural and industrial effluents along Al-Gabal Al-Akhdar coast, Libya. According to Soliman et al. (2015), Cd showed low concentrations among individual metals (Fe, Pb, Mn, Ni, Zn, Cr, Cu, Co and Cd) in 14 sites along the Libyan coastline but it was the only metal to show very high contamination levels in regard to CF guideline values. Soliman et al. (2015) also found evidences that Mn, Cu, Cd, Zn, Co and Ni have similar sources and/or the same geochemical processes that control their levels in sediments.

The elevated metal levels in samples of site 1 followed by site 3, in comparison to site 2 and site 4, may be attributed to the high load of untreated pollutants that are released directly at these lagoons and the general increase of anthropogenic activities as well. Several studies confirmed the anthropogenic origin of Cd, Pb, Cu and Zn such as household wastes, exhaust emissions, municipal effluents, shipping activities, antifouling paints, phosphate fertilizers and pesticides, and many others. In fact, Cd and Pb specifically originate mainly from anthropogenic activities and their natural sources of emission are rare (Ungureanu et al., 2016; Guan et al., 2018).

DOI: http://dx.doi.org/10.15666/aeer/2002_13991412

The present work confirms the potential ecological risks posed by Cd among other studied metals due to various anthropogenic activities along major Libyan cities such as Benghazi and Tobruk. Similar results were reported in the Mediterranean coast of Sfax City, Tunisia (Houda et al., 2011), in Manzala Lake, Egypt (Zahran et al., 2015), in the Red Sea coast of Hodeida, Yemen Republic (Omar et al., 2016) and in 9 sites along Yemen's Red Sea coast (Saleh, 2021).

Conclusion

The continued uncontrolled discharge of domestic, industrial and agricultural effluents to the aquatic ecosystems in large cities such as Benghazi and Tobruk proved to be of critical concern and may disrupt natural attenuation mechanisms. The utilization of CF, EF, mC_d, PLI and I_{geo} and other sediment pollution indices proved to be efficient in surveying and monitoring the pollution conditions of marine ecosystems with variable and complex pollution gradients. Comprehensive metal risk assessment measures act as early warning of any expected potential risks at densely populated areas, thus continuous and periodic contaminant assessment surveys are recommended.

Acknowledgment. The authors would like to acknowledge Taif University Researchers Supporting Project Number (TURSP-2020/44), Taif University, Taif, Saudi Arabia.

Declaration of competing interests. The authors declare no conflict of interests.

Authors contributions. Wael A. Omar performed the sample processing, measurements also conducted the writing and editing of the manuscript. Mariam A. Busaadia conducted the practical work, sample collection, sample preparation and participated in writing and editing the manuscript. Yousef S. Saleh and Abdulraheem S.A. Almalki conducted the data processing, statistical analysis as well as preparation of tables and figures. Mohamed-Assem S. Marie reviewed and edited the final version of the manuscript. The present work was performed as a continuation of the survey conducted along the northeastern coast of Libya as partial fulfillment of the requirements for the Ph.D. Degree of Science awarded by Cairo University to Mariam A. Busaadia under supervision of Wael A. Omar and Mohamed-Assem S. Marie.

Ethical approval. All procedures performed in the present study did not involve human or animal participants.

REFERENCES

[1] Abdel-Ghani, S. A. (2015): Trace metals in seawater, sediments and some fish species from Marsa Matrouh Beaches in north-western Mediterranean coast. Egypt. – The Egyptian Journal of Aquatic Research 41: 145-154.
[2] Abrahim, G. M. S., Parker, R. J. (2008): Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. – Environmental Monitoring and Assessment 136(1-3): 227-238.
[3] Alhadhrami, A., Adam, A. A., Almalki, A. S. A., Refat, M. S. (2019): Synthesis of Iron (III) oxide nanoparticles via simple and cheap procedures for adsorption of environmentally harmful toxic heavy metals. – Revue Roumaine de Chimie 64(9): 817-828.
[4] Al-Hassan, L. A. J. (1999): First record of some fishes from Libyan waters. – Indian Journal of Fisheries 46(2): 195-198.

[5] Ali, M. H., Abdel-Satar, A. M. (2005): Studies of some heavy metals in water, sediment, fish and fish diets in some fish farms in El-Fayoum province, Egypt. – Journal of Aquatic Research 31: 261-273.

[6] APHA (American Public Health Association) (2005): Standard methods for the examination of water and wastewater. – American Water Works Association, New York, USA.

[7] Birch, G. F. (2017): Determination of sediment metal background concentrations and enrichment in marine environments - A critical review. – Science of the Total Environment 580: 813-831.

[8] Birch, G. F., Olmos, M. A. (2008): Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies. – ICES Journal of Marine Science 65: 1407-1413.

[9] Buat-Menard, P., Chesselet, R. (1979): Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. – Earth and Planetary Science Letters 42: 399-411.

[10] Cabrera, F., Conde, B., Flores, V. (1992): Heavy metals in the surface sediments of the tidal river Tinto (SW Spain). – Fresenius Environmental Bulletin 1: 400-405.

[11] Ergin, M., Saydam, C., Baştürk, Ö., Erdem, E., Yörük, R. (1991): Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the northeastern Sea of Marmara. – Chemical Geology 91: 269-285.

[12] Guan, J., Wang, J., Pan, H., Yang, C., Qu, J., Lu, N., Yuan, X. (2018): Heavy metals in Yinma River sediment in a major Phaeozems zone, Northeast China: Distribution, chemical fraction, contamination assessment and source apportionment. – Scientific Reports 8(1): 12231.

[13] Haddoud, D. A., Rawag, A. A. (2007): Marine protected areas along Libyan coast. – In: Report of the MedSudMed expert consultation on marine protected areas and fisheries management. MedSudMed Technical Documents No. 3, Rome (Italy) (GCP/RER/010/ITA/MSM-TD-03), pp. 23-31.

[14] Hakanson, L. (1980): An ecological risk index for aquatic pollution control. A sedimentological approach. – Water Research 14(8): 975-1001.

[15] Hamouda, M. S., Wilson, J. G. (1989): Levels of heavy metals along the Libyan coastline. – Marine Pollution Bulletin 20(12): 621-624.

[16] Hasan, H. M. I., Ul Islam, M. (2010): The concentrations of some heavy metals of Al-Gabal Al-Akhdar coast sediment. – Archives of Applied Science Research 6: 59-67.

[17] Houda, B., Dorra, G., Chafai, A., Emna, A., Khaled, M. (2011): Impact of a mixed industrial and domestic wastewater effluent on the southern coastal sediments of Sfax (Tunisia) in the Mediterranean Sea. – International Journal of Environmental Research 5(3): 691-704.

[18] Hseu, Z. Y. (2004): Evaluating heavy metal contents in nine composts using four digestion methods. – Bioresource Technology 95: 53-59.

[19] Issac, R. A., Kerber, J. D. (1971): Atomic absorption and flame photometry. Techniques and uses in soil, plant and water analysis. – In: Walsh, L. M. (ed.) Instrumental Methods for Analysis of Soil and Plant Tissue. Soil Science Society of America-Agronomy Society of America, Inc, Madison, WI, USA, pp. 17-37.

[20] Karbassi, A. R., Monavari, S. M., NabiBidhendi, G. R., Nouri, J., Nematpour, K. (2008): Metal pollution assessment of sediment and water in the Shur River. – Environmental Monitoring and Assessment 147(1-3): 107-116.

[21] Kerambrun, P. (1986): Coastal lagoons along the southern Mediterranean coast (Algeria, Egypt, Libya, Morocco, Tunisia) description and bibliography. – UNESCO reports in Marine Science, 34, UNESCO, Paris.

[22] Long, E. R., MacDonald, D. D., Smith, S. L., Calder, F. D. (1995): Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. – Environmental Management 19(1): 81-97.

[23] Long, E. R., MacDonald, D. D., Severn, C. G., Hong, C. B. (2000): Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. – Environmental Toxicology and Chemistry 19(10): 2598-2601.

[24] Lu, X., Wang, L., Lei, K., Huang, J., Zhai, Y. (2009): Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China. – Journal of Hazardous Materials 161: 1058-1062.

[25] MacDonald, D. D., Ingersoll, C. G., Berger, T. A. (2000): Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. – Archives of Environmental Contamination and Toxicology 39(1): 20-31.

[26] Metwally, M. A. A., Fouad, I. M. (2008): Biochemical changes induced by heavy metal pollution in marine fishes at Khomse coast, Libya. – Global Veterinaria 2(6): 308-311.

[27] Müller, G. (1969): Index of geoaccumulation in the sediments of the Rhine River. – GeoJournal 2: 108-118.

[28] Omar, W. A., Saleh, Y. S., Marie, M-A. S. (2016): The use of biotic and abiotic components of Red Sea coastal marine areas as indicators of ecosystem health. – Ecotoxicology 25: 253-266.

[29] Paudel, P. N., Pokhrel, B., Kafle, B. K., Gyawali, R. (2016): Analysis of heavy metals in some commercially important fishes of Kathmandu Valley, Nepal. – International Food Research Journal 23(3): 1005-1011.

[30] Rakib, Md. R. J., Jolly, Y. N., Enyoh, C. E., Khandaker, M. U., Hossain, M. B., Akther, S., Alsubaie, A., Almalki, A. S. A., Bradley, D. A. (2021): Levels and health risk assessment of heavy metals in dried fish consumed in Bangladesh. – Scientific Reports 11(14642): 1-13.

[31] Sadauskas-Henrique, H., Sakuragui, M. M., Paulino, M. G., Fernandes, M. N. (2011): Using condition factor and blood variable biomarkers in fish to assess water quality. – Environmental Monitoring and Assessment 181: 29-42.

[32] Saleh, Y. S. (2021): Evaluation of sediment contamination in the Red Sea coastal area combining multiple pollution indices and multivariate statistical techniques. – International Journal of Sediment Research 36: 243-254.

[33] SAS (Statistical Analysis System) (2006): SAS/STAT User's Guide, Version 9.1. – SAS Institute Inc., Cary, NC, USA.

[34] Soliman, N. F., Nasr, S. M., Okbah, M. A., El Haddad, H. S. (2015): Assessment of metals contamination in sediments from the Mediterranean Sea (Libya) using pollution indices and multivariate statistical techniques. – Global Journal of Advanced Research 2: 120-136.

[35] Tomlinson, D. L., Wilson, J. G., Harris, C. R., Jeffrey, D. W. (1980): Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. – Helgoläander Meeresuntersuchungen 33(1): 566-575.

[36] Tornero, V., Hanke, G. (2016): Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas. – Marine Pollution Bulletin 112: 17-38.

[37] Turekian, K. K., Wedepohl, K. H. (1961): Distribution of the elements in some major units of the Earth's crust. – Bulletin of the Geological Society of America 72: 175-192.

[38] Ungureanu, T., Iancu, G. O., Pintilei, M., Chicos, M. M. (2016): Spatial distribution and geochemistry of heavy metals in soils: A case study from the NE area of Vaslui county, Romania. – Journal of Geochemical Exploration 176(1): 20-32.

[39] Wang, J., Liu, R. M., Zhang, P. P., Yu, W. W., Shen, Z. Y., Feng, C. H. (2014): Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary. – Marine Pollution Bulletin 87: 364-373.

[40] WHO (World Health Organization) (2017): Guidelines for drinking-water quality: 4th edition incorporating the first addendum. – Geneva, World Health Organization.

[41] Xu, Z. Q., Ni, S., Tuo, X. G., Zhang, C. J. (2008): Calculation of heavy metal's toxicity coefficient in the evaluation of potential ecological risk index. – Environmental Science and Technology 31(2): 112-115.

[42] Yi, Y. J., Yang, Z. F., Zhang, S. H. (2011): Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. – Environmental Pollution 159: 2575-2585.

[43] Yu, R., Yuan, X., Zhao, Y., Hu, G., Tu, X. (2008): Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. – Journal of Environmental Sciences 20(6): 664-669.

[44] Zahra, A., Hashmi, M. Z., Malik, R. N., Ahmed, Z. (2014): Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-Feeding tributary of the Rawal Lake Reservoir, Pakistan. – Science of the Total Environment 470-471: 925-933.

[45] Zahran, M. A. E., El-Amier, Y. A., Elnaggar, A. A., Mohamed, H. A. E., El-Alfy, M. A. E. (2015): Assessment and distribution of heavy metals pollutants in Manzala Lake, Egypt. – Journal of Geoscience and Environment Protection 3(6): 107-122.

[46] Zhang, H., Feng, W., Chang, J., Qu, J., Xie, H., Yu, L. (2009): Heavy metal concentration in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. – Environmental Pollution 157(5): 1533-1543.