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Assessment of metals contamination in sediments from the Mediterranean Sea (Libya) using pollution indices and multivariate statistical techniques

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ABSTRACT

Total metals concentrations, Geoaccumulation index (Igeo), Pollution load index (PLI), degree of contamination (DC) and sediment quality guidelines (SQGs) were used to assess heavy metals contamination status and ecological risk in the sediments from the Libyan Mediterranean coast. The distribution pattern of heavy metals in the sediment follows the sequence: Fe>Pb>Mn>Ni>Zn>Cr>Cu>Co>Cd. Over than 100% of the samples were lower than the Cr and Zn thresholds effect level (TEL) of SQGs, 79% percent of sediments would be expected to occasionally be associated with the toxic adverse effects on aquatic organisms because of Pb. While, cadmium exceeded the probable effect level (PEL) value at 100% of the sediment samples. In general, the results revealed very high contamination factor ($C_f > 6$) for Cd. This was supported by CF (>6) for Cd. The modified degree of contamination was ($4 \leq mC_d < 8$), reflecting high degree of contamination. The calculated PLI were less than 1, indicating only baseline levels of pollution. Multivariate statistical analyses (Principal component analysis, cluster analysis) and correlation matrix were used in this study. Highly significant correlations were found between the concentrations of Cd, Co, Cu, Mn, Ni and Zn, suggesting similar sources and/or similar geochemical processes controlling the occurrence of these metals in the sediments. The study point out that although there were slight variations in the results of the three indices, the combination of the three indices gave us a comprehensive understanding of heavy metals risks in the surface sediments of the Libyan Mediterranean coast.

Keywords

Sediment, Geoaccumulation index, Pollution load index, Modified degree of contamination, Sediment Quality Guidelines

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1. INTRODUCTION

Rapid industrialization and uncontrolled urbanization around many cities and coastal area have brought alarming level of pollutions to the aquatic environments because of their anthropogenic inputs. Heavy metals are considered as serious inorganic pollutants because of their toxic effects on life in aquatic system, having a high enrichment factor and slow removal rate (Alloway and Ayres, 1997). As a consequence, it is assumed that the equilibrium balance between the metals in sediments and surface water is disrupted that might be a reason to increase water contamination (Rahman et al., 2013).

Sediment as a compartment is more conservative than water, as it accumulates historical data on processes within water bodies and the effect of anthropogenic factors on these processes. For these reasons, sediment quality parameters have been used as environmental indicators and their ability to trace and monitor contamination sources is largely recognized (Vallejuelo et al., 2010).

Libyan coastline is considered as the longest African coastline on the Mediterranean Sea. In addition to its length, it is in the same time very rich in its natural resources in the field of fish wealth or energy and mineral raw resources. A study of the distribution, enrichment and accumulation of metals in the Libyan Mediterranean coastal sediments is important to the assessment of the possible influence of anthropogenic activities on sea water. However, the recent available information lacked sufficient and adequate accuracy and details (Hamouda and Wilson, 1989 and Hasan and Islam, 2010). An assessment is thus necessary to appraise the concentration of metals in different coastal areas along the Libyan Mediterranean coastline so as to understand the present condition of the coastline and to compile the baseline data for future monitoring.

The objectives of this study were: i) to examine the spatial variations of the heavy metal concentration in the surface sediment of the Libyan Mediterranean coast, ii) to define the natural and/or anthropogenic sources of these metals using multivariate statistical technique, iii) to explore the degree of heavy metal contamination using different pollution indices, iv) to assess environmental risks of heavy metals in the study area by comparison with sediment quality guidelines (SQGs).

2. MATERIALS AND METHODS

Study area

Libya has a unique position in the middle of North Africa. It is a junction between its eastern and western seashores. It embraces the southern coasts of the Mediterranean Sea, forming the heart for this great sea. The Libyan Coast extends to about 1900Km between Beir Al Ramla on the Egyptian borders to the east and Ras Gidier on the Tunisian borders to the west (Fig. 1).

This distance is equal to around 37% of the total Arab Coasts on the Mediterranean Sea. The Libyan coastline is considered as the longest African coastline on the Mediterranean Sea. In addition to its length, it is in the same time very rich in its natural resources be they in the field of fish wealth or energy and mineral raw resources (El Haddad, 2012).

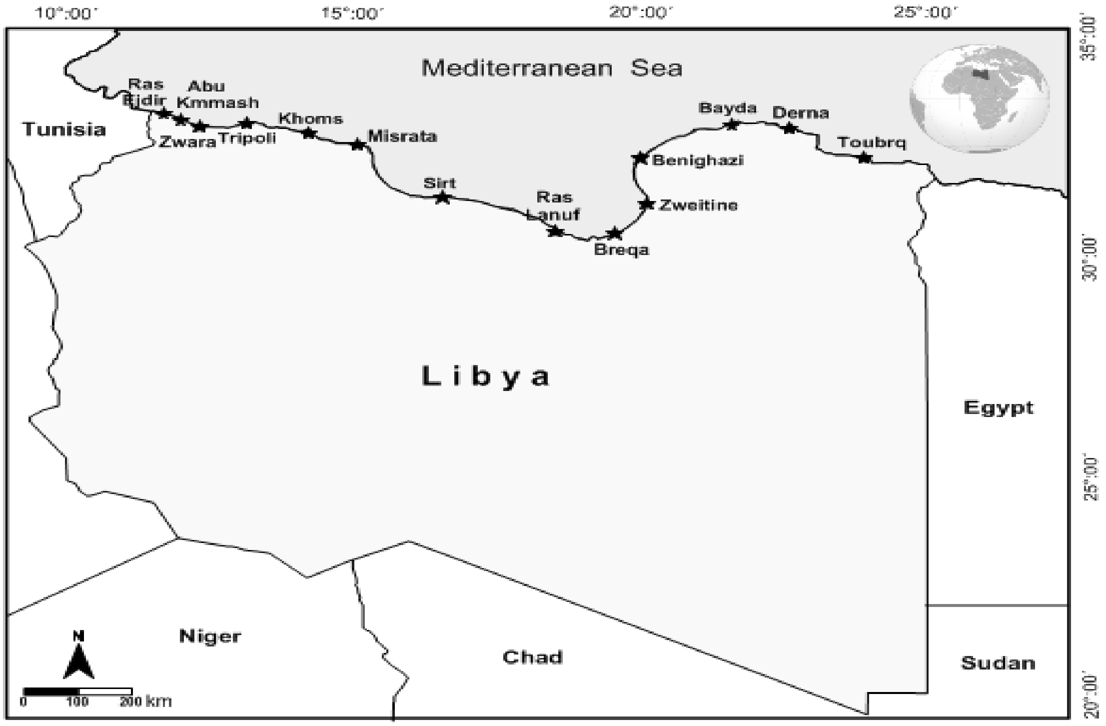

Figure 1: Sampling locations of the study area

Collection and preparation of samples

Fourteen surface sediment samples (0-5 cm) were collected from the coastal zone of Libya using grab sampler (Fig. 1). The sampling stations were chosen carefully to provide good area coverage. After sampling, the sediments were stored in a plastic vessel and frozen at -20ºC. In the laboratory, the sediments were defrosted at room temperature, dried at 40ºC to constant weight, and ground and homogenized in a mortar to a fine powder.

Metal analysis

The samples were digested in an open system with a mixture of concentrated HNO_3/ $HClO_4$/ HF (3:2:1) according to Oregioni and Aston (1984). The determination of the metals in the sediment samples were performed with a SHIMADZU AA6800 atomic absorption spectrophotometer equipped with a deuterium background corrector. An atomizer with an air/acetylene burner was used for determining all the investigated elements. All instrumental settings were those recommended in the manufacturer's manual book. Suitable internal chemical standards (Merck Chemicals, Germany) were used to calibrate the instrument.

Quality control

To remove any contamination, all glassware and plastic vials were washed with 10% nitric acid solution and rinsed thoroughly with Milli-Q water and dried. All reagents were Merck analytical grade or super pure quality. In order to check for the quality of the method applied for the analysis of heavy metals, the accuracy of the analytical method was estimated by analyzing sediment Standard Reference Material (IAEA-405): estuarine sediment, International Atomic Energy Agency, Vienna, Austria). The recovery of the selected metals ranged from 90 to 104% and the measurements of precision was under 10% RSD.

Statistical analysis

Minitab 14 and SPSS 16 software were used in the present study for the calculation of Pearson Correlation coefficient matrix, Factor analysis and constructing a dendrogram for the Hierarchical Cluster analysis.

3. RESULTS AND DISCUSSION

3.1. Characteristics of sediments

Table 1 show that the studied sediments contain high sand fractions (30.79-92.59%). This indicates that the sand is the dominant component in the collected samples. Additionally, the sum of silt and clay fractions fluctuates between 0.40 and 8.70%. Organic matter (OM) content was low, ranging from 0.82 % at Khoms to 1.91% at Benghazi. The results showed differences in the distribution of $CaCO_3$%. The western region was characterized by relatively medium $CaCO_3$ while the eastern region was characterized by high percentage of $CaCO_3$. These results are in agreement with the results of Hamouda and Wilson (1989).

3.2. Heavy metals distribution

The range and mean heavy metal concentrations in surface sediments of the Libyan Mediterranean coast are summarized in Table 2. The mean value of heavy metals concentrations in the study area follows a descending order as: Fe>Pb>Mn>Ni>Zn>Cr>Cu>Co>Cd.

A comparative study between metal concentrations in sediments of the Libyan Mediterranean coast with those of other regions along the Mediterranean (Table 3) revealed that the sediments of the Libyan coast have higher concentrations of Cd while, Fe, Mn, Ni, and Zn have lower concentrations than those of other regions. Concentrations of Pb were lower than those measured in Pasajaes harbor, Coast of Safax, Taranto Gulf, Sardina, Naples harbor, Thermaikos Gulfs and Mediterranean Sea of France and higher than those reported in the Algeciras bay and the Mediterranean coast of Algeria, Morocco and Egypt. However, Cr and Cu showed values higher than those measured in the Mediterranean coast of Algeria. Finally, Co showed lower concentrations than those reported in Algeciras Bay and Mediterranean Sea of Egypt.

Table 1: Physicochemical characteristics of sediments along the Libyan Mediterranean coast.

Sites	Lat.	Long.	O.M.%	CaCO3%	Grain size analysis	
					Sand%	Silt%+Clay
Toubrk	32° 04' 886" N	24° 00' 215"E	1.72	90.54	92.20	7.80
Derna	32° 05' 460" N	23° 57'489" E	1.53	92.06	96.20	3.80
Bayda	32° 55' 082" N	21° 37' 422"E	1.61	91.11	99.50	0.50
Benghazi	32° 06' 044" N	20° 03' 114" E	1.91	90.13	96.20	3.80
Zweitine	30° 56' 456" N	20° 06' 299" E	1.76	92.59	98.60	1.40
Brega	30° 23' 553"N	19° 37' 521" E	1.63	91.25	95.60	4.40
Ras Lanuf	30° 36' 719' N	18° 21' 880" E	1.14	84.72	96.50	3.50
Sirt	32° 06' 138" N	20° 05' 767" E	1.52	83.38	99.60	0.40
Misurata	32° 26' 270" N	14° 54' 261" E	1.48	47.67	95.60	4.40
Khoms	32° 56' 448" N	12° 03' 954" E	0.82	30.79	96.80	3.20
Tripoli	32° 26' 262" N	14° 54' 259" E	1.23	44.38	93.60	6.40
Zwara	32° 57'318" N	12° 03' 133" E	1.38	74.85	91.30	8.70
Abu Kmmash	33° 04' 725" N	11° 48' 784" E	1.23	53.70	95.70	4.30
Ras Ejdir	34°81' 757" N	12° 58' 797" E	0.86	55.68	92.40	7.60

Table 2: Sediment quality values for trace metals (in μgg^{-1} dry wt) for marine sediments, and the values obtained in the present study, Libya.

Sites	Fe	Mn	Cu	Zn	Ni	Cr	Co	Pb	Cd
Min.	141.8	14.3	9.1	11.6	11.6	14.8	8.2	18.9	5.0
Max.	1056.8	49.4	22.7	30.5	29.9	24.9	18.1	56.9	10.5
Mean	571.4	28.6	15.4	20.1	22.2	18.7	13.9	36.6	8.3
SD	272.3	11.1	4.7	5.9	6.9	3.8	4.1	11.2	2.4
PEL	NA	NA	108.20	271.00	42.80	160.40	NA	112.18	4.21
TEL	NA	NA	18.70	124.00	15.90	7.24	NA	30.20	0.68

NA; Not available

TEL; Threshold effect level

PEL; probable effect level

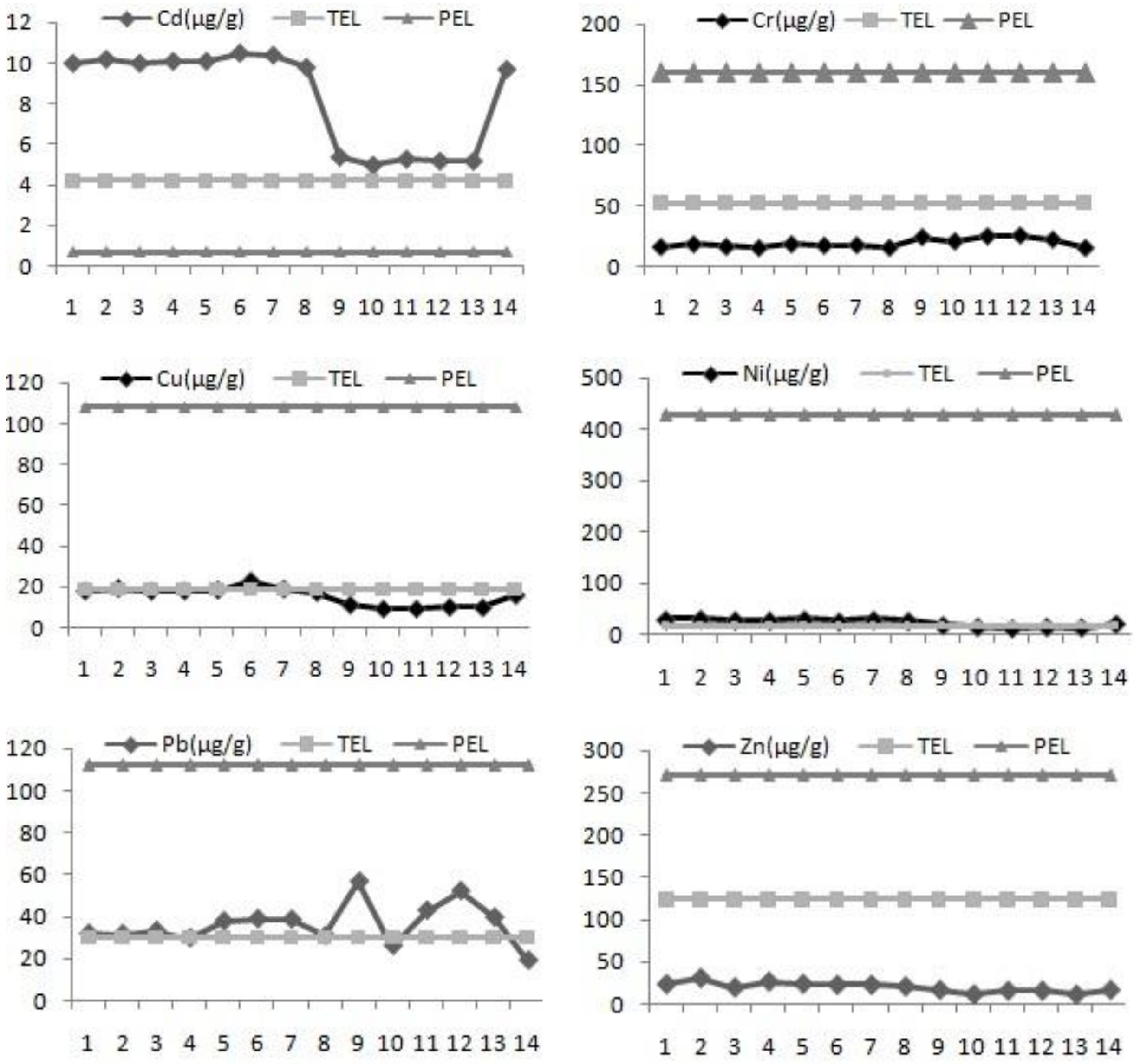

Figure 2: Distribution of each heavy metal concentration (µg/g) along the Libyan Mediterranean coast

Table 3: Heavy metal concentrations in sediment samples from the Libyan Mediterranean coast and other selected regions along the Mediterranean Sea.

Location	Cd	Cu	Cr	Co	Fe	Mn	Ni	Zn	Pb
This study	5-10.5	9.1-22.7	14.8-24.9	8.2-18.1	141.8-1056.8	14.3-49.4	11.6-29.9	11.6-30.5	18.9-56.9
The eastern Libyan coast[a]	ND-1.73	8.7-42	NA	NA	NA	37-76.7	5.7-19	2.3-27.3	NA
Egyptian Med. Coast[b]	0.04-0.47	0.46-26	4.1-297	0.43-26.39	243.5-38045.1	17.3-1086	1.7-60	2.05-62	3.34-53
Pasajes harbour, Spain[c]	1.2-6.64	25-3726	NA	NA	3830-35500	64-365	17-99	477-1390	45-346
Coast of Safax[d]	5.5-7	13-29	41-82	NA	41011-50163	NA	7-55	39-117	18-88
Taranto Gulf, Italy[e]	NA	42.4-52	75.2-102	NA	26313-36098	552-2826	47-60	86.8-129	44.7-74
Nables Harbour, Italy[f]	0.2-2.5	40-415	10.3-161	1.9-7.2	NA	95-535	NA	41-1196	37-314
Algeciras Bay, Spain[g]	0.1-22	5-25	30-251	5-22	18285-42756	235-967	19-144	33-117	12-39
Mediterranean Sea, Algeria[h]	0.1-2.3	1.1-10	2.6-18	NA	NA	NA	0.8-54	5.3-45.7	1.3-11
Mediterranean Sea, France[i]	0.15-3.4	14.82	NA	NA	NA	NA	NA	29.4-509	20.1-393
Sardina, Italy[j]	0.21-13	2.77-51	NA	NA	NA	NA	0.9-51	198-3239	74-772
Themaikos Gulf, Greece[k]	0.3-8.4	32-130	21-470	NA	NA	590-890	63-130	84-537	38-190
Moroccan Med. Coast[l]	0.03-0.25	1.2-6	NA	NA	NA	NA	NA	9.2-37	0.17-0.25

NA; Not available
[a] Hasan and Islam, 2010
[b] Okbah et al., 2014
[c] Legoburu, I. and Canton, L. 1991.
[d] Gargouri et al., 2010
[e] Buccolieri et al., 2006
[f] Adamo et al., 2005
[g] Dias de Alba et al., 2011
[h] Alomary and Belhadj, 2007
[i] Femex et al., 2001
[j] Caredda et al., 1999
[k] Violintzis et al., 2009
[l] Sabhi et al., 2000

3.3. Sediment Quality Guidelines

Numerous sediment quality guidelines are used to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants (McCready et al., 2006). These sediment quality guidelines are most widely used to assess the ecotoxicology of sediments. This approach is based on the relation between measured concentrations of metals and observed biological effects, such as mortality, growth or reproduction of living organisms. Threshold effect level (TEL) refers to the concentration below which adverse effects are expected to occur only rarely and probable effect level (PEL) indicates the concentration above which adverse effects are expected to occur frequently (Saleem et al., 2013). These levels were established by the Canadian Council of Ministers of the Environment, and are routinely used as screening tools by different stakeholders who involved in sediment management activities (Anonymous, 2002). The sediments quality guidelines for the selected metals and a classification of the samples based on the guidelines are shown in Table 2 and Fig. 2. When compared to the TEL-PEL SQGs, the measured levels of Cr and Zn were found to be lower than TEL and PEL values at 100% of sampling stations. On the other hand, in case of Ni, 21% of samples fall in the range between TEL and PEL at Derna, Berga and Ras Lanuf indicating associated adverse biological effects may occasionally occur. About 50% of samples are higher than TEL and lower than PEL values of Ni at Tobruk, Derna, Beath, Benghazi, Zweitine, Berga, Ras Lanuf, Sirt, Misurata, and Tripoli. The measured levels of Pb in most of the sediment samples (79%) exceeded the TEL value at Tobruk, Derna, Beath, Zweitine, Berga, Ras Lanuf, Sirt, Misurata, Tripoli, Zwara and Abu kmmash). Among the studied elements, cadmium is the only metal that exceeds the PEL value at 100% of the sediment samples. Accordingly, it appears that the Libyan Mediterranean coastal sediments are contaminated with cadmium. The high content is mainly attributed to the brackish effluents. The association of Cd with carbonate is reported. Cd in sediments is less mobile than other metals due to the formation of $CdCO_3$ phases in alkaline media (Hasan and Islam, 2010).

Although background/reference concentrations do give a base to evaluate SQGs and are important in environmental studies, they provide little insight into the potential ecological impact of contaminants (Gao et al., 2012). Based on the fact that heavy metals always occur in sediments as complex mixtures, the mean PEL quotient method has been applied to determine the possible biological effect of combined toxicant groups by calculating mean quotients for a large range of contaminants using the following equation:

$$m-PEL-Q=\left(\sum_{i=1}^{n}PEL-Q_i\right)\Big/n_i$$

$$PEL-Q_i=C_i/PEL_i$$

where *m-PEL–Q* is the mean *PEL* quotient of multiple metal contamination, C_i is the total content of selected metal ‘‘*i*’’, *PELi* is the *PEL* value of selected metal ‘‘*i*’’, and ‘‘*n*’’ is the number of selected metals. The *m-PEL–Q* values of <0.1, 0.11-1.5, 1.51-2.3 and >2.3 related to the likelihood that 10%, 25%, 50% and 76% of sediments with these PELQ values, respectively, were toxic in amphipod survival bioassays. Consequently, four relative level of priority (highly toxic, medium toxic, slightly toxic and non toxic) have been proposed. The *m-PEL–Q* in surface sediments of the Libyan Mediterranean coast range from 1.31 to 2.71 (mean value of 2.16) (Fig.3), indicating that the combination of Cd, Cr, Cu, Ni, Pb and Zn may have a 50% probability of being toxic.

Furthermore, potential acute toxicity of contaminants in sediment samples could be estimated as the sum of the toxic units (∑TUs) defined as the ratio of the determined concentration to PEL value. In Fig. 4, the values of sum of TUs for each sampling stations based on the concentrations of Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn were shown. The sum of the toxic unit at Derna, Berga, and Ras Lanuf exhibit higher levels than other stations.

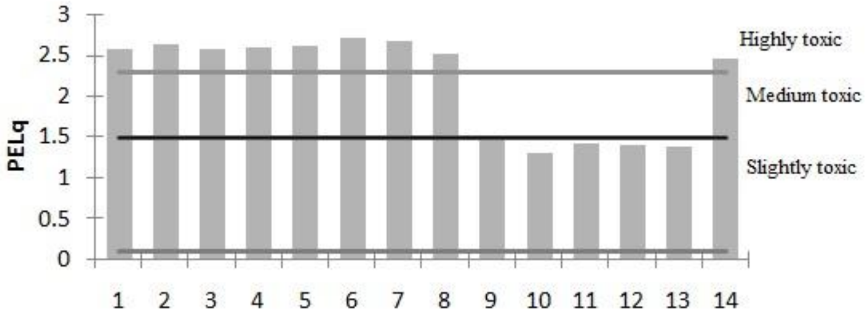

Figure 3: Estimated mean PELq of surface sediments from the Libyan Mediterranean coast

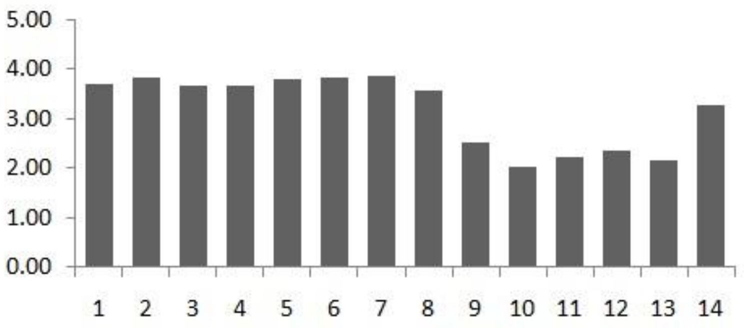

Figure 4: Estimated sum of the toxic units (∑TUs) of surface sediments from the Libyan Mediterranean coast

3.4. Assessment of sediment contamination

A number of methods have been put forward for quantifying the degree of metal enrichment in sediments. Various authors (Tomlinson et al., 1980; Muller, 1969; Hakanson, 1980) have proposed pollution impact ranges to convert the calculated numerical results into broad descriptive bands of pollution ranging from low to high intensity (Abrahim and Parker, 2008). In this study, three different indices were used to assess the degree of heavy metal contamination in sediments of the Libyan coast.

The geoaccumulation index (*Igeo*):

The geoaccumulation index (Igeo) originally introduced by Müller (1969), determine and define metal contamination in sediments. The geoaccumulation index (Igeo) is defined by the following equation:

$$I_{geo} = \log_2 \left(C_n / 1.5 x B_n \right)$$

where C_n is the measured concentration of the examined metal (n) in the sediment and B_n is the geochemical background concentration of the metal (n). The factor 1.5 is the background matrix correction factor due to lithological variability. The background values of the metals here are the same as those recorded in the enrichment factor calculation. Similar to metal enrichment factor, geoaccumulation index can be used as a reference to estimate the extent of metal pollution (Zhang et al., 2009). Müller has distinguished seven classes of the geoaccumulation index from Class 0 (Igeo=0) to Class

6 (Igeo>5). The Igeo is associated with a qualitative scale of pollution intensity, samples may be classified as unpolluted (Igeo≤0), unpolluted to moderately polluted (0≤Igeo≤1), moderately polluted (1≤Igeo≤2), moderate to strongly polluted (2≤Igeo≤3), strongly polluted (3≤Igeo≤4), strongly to extremely polluted (4≤Igeo≤5), and extremely polluted (Igeo≥5).

The geo-accumulation indexes calculated for the sediments are summarized in Figure 5 in the form of a Box Whiskers plot. According to Muller's scale, the mean geo-accumulation indexes of Cr (-2.88), Co (-0.56), Cu (−2.21), Fe (−7.18), Mn (−5.59), Ni (−2.28), and Zn (−2.89) are less than zero (Igeo<0), suggesting that the Libyan Mediterranean Sea has not been polluted overall by these metals. The Igeo class of Pb was under 1 in the sediments of all sites which usually had "unpolluted to moderately polluted" class. Among the studied elements, Cd had the highest mean Igeo values (4.13), suggesting the sediments has been strongly to very strongly polluted with this metal.

Contamination factors (CF) and Degree of contamination (Dc)

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by baseline of background value.

$$C_f = M_x / M_b$$

CF value were interpreted as suggested by Hakanson (1980), where: CF < 1 indicates low contamination; 1<CF<3 is moderate contamination; 3<CF<6 is considerable contamination; and CF>6 is very high contamination.

The results of contamination factors (Table 4) indicated that in the Libyan Mediterranean coast Ni, Zn, Fe, Cu, Mn and Cr possess the lowest CFs reflecting lowest contaminated sediments (CF<1). Both Pb and Co showed low to moderate contamination level of contamination. On the other hand, Sediments of all sites are highly contaminated (CF>6) with Cd.

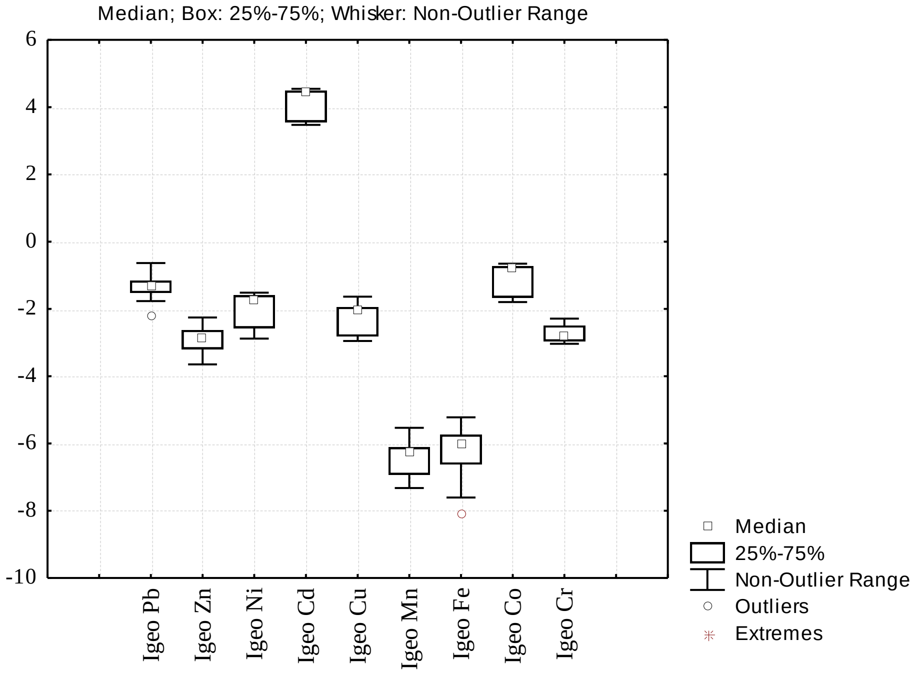

Figure 5: Box plot for the values of Igeo in the Libyan Mediterranean coast.

The overall degree of contamination is given by:

$$C_d = \sum_{i=1}^{8} C_f^i$$

Since it is not always feasible to analyze all of the components used for this index, a variation of this method was proposed by Abrahim and Parker (2008) providing the modified degree of contamination (mC_d) using the following equation:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \qquad (5)$$

Where n = number of analysed elements and i = ith element and C_f = contamination factor

Using this generalized formula to calculate the mC_d allows the incorporation of as many metals as the study may analyze with no upper limit. Classification of the sediments according to the modified degree of contamination is as follows: mCd < 1.5 Nile to very low degree of contamination; $1.5 \le mC_d < 1.5$ Low degree of contamination; $2 \le mC_d < 4$ Moderate degree of contamination; $4 \le mC_d < 8$ High degree of contamination; $8 \le mC_d < 16$ Very high degree of contamination; $16 \le mC_d < 32$ Extremely high degree of contamination; $mC_d \ge 32$ Ultra high degree of contamination.

The modified degree of contamination (mC_d) was calculated to produce an overall average value for a range of pollutants. The modified degree of contamination (mC_d) for the sediments of the study area is shown in Table 4. The Libyan Mediterranean coastal sediments showed mC_d values ranging from 4.05 to 8.35 reflecting high degree of contamination.

Pollution Load index (PLI)

For the entire sampling sites, PLI has been determined as the nth root of the product of the n CF:

$$\text{PLI} = (\text{CF1 x CF2 x CF3 x ….x CFn})^{1/n}$$

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI>1, it means that a pollution exists; otherwise, if PLI<1, there is no metal pollution (Tomlinson et al., 1980).

The pollution load index (PLI) ranged from 0.29 to 0.50. According to the mean PLI value (0.42), the Libyan Mediterranean coast was unpolluted.

Table 4: Metal contamination factors (CFs) and pollution load indices (PLIs) for sediments of the Libyan Mediterranean coast.

	CF Pb	CF Zn	CF Ni	CF Cd	CF Cu	CF Mn	CF Co	CF Cr	Sum CF	mCd	PLI
1	1.67	0.25	0.55	58.82	0.54	0.04	1.19	0.22	63.28	7.91	0.47
2	1.66	0.32	0.58	60.00	0.58	0.06	1.23	0.25	64.68	8.08	0.45
3	1.74	0.21	0.53	58.82	0.54	0.05	1.21	0.22	63.32	7.92	0.49
4	1.56	0.28	0.52	59.41	0.54	0.04	1.18	0.21	63.74	7.97	0.48
5	1.99	0.25	0.56	59.41	0.55	0.04	1.24	0.25	64.30	8.04	0.50
6	2.05	0.24	0.49	61.76	0.69	0.02	1.29	0.23	66.77	8.35	0.45
7	2.03	0.24	0.54	61.18	0.57	0.04	1.28	0.24	66.12	8.27	0.50
8	1.62	0.22	0.51	57.65	0.52	0.04	1.16	0.21	61.92	7.74	0.45
9	2.99	0.18	0.34	31.76	0.34	0.04	0.69	0.33	36.67	4.58	0.38
10	1.37	0.12	0.28	29.41	0.28	0.04	0.60	0.28	32.37	4.05	0.30
11	2.26	0.17	0.22	31.18	0.28	0.02	0.59	0.34	35.05	4.38	0.29
12	2.76	0.17	0.28	30.59	0.30	0.02	0.64	0.35	35.10	4.39	0.36
13	2.08	0.12	0.26	30.59	0.29	0.02	0.62	0.30	34.29	4.29	0.33
14	0.99	0.18	0.39	57.06	0.48	0.03	1.06	0.21	60.39	7.55	0.38

3.5. Multivariate Statistical analysis

Multivariate analysis (i.e. Principal component analysis; PCA and Cluster analysis; CA) has been proved to be an effective tool for providing suggestive information regarding heavy metal sources and pathways (Hu et al., 2013).

Correlation matrix

In order to establish relationships among metals and determine the common source of metals in the Libyan Mediterranean coast, a correlation matrix was calculated for heavy metals in the sediments. According to the values of Pearson correlation coefficients (Table 5), a significant positive correlation existed among the metals studied. In this study, Cd was significantly correlated with Co, Cu, Mn, Ni and Zn. It indicated strong association of these metals in the sediments where they might be share common sources (Saleem et al., 2013). The significantly positive correlation of Cu (r=0.766, p<0.01) and Pb (r=0.66, p<0.01) suggested that these metals were redistributed in the sediments by the same physico-chemical processes or had a similar source (Bai et al., 2011). The major role of carbonate as metal carrier is reflected by the positive correlations between Cd, Co, Cu, Mn, Ni, and Zn with $CaCO_3$. On the other hand, the positive correlation of OM with Ni and Cu suggested that OM has an important role in the binding of these elements. The negative correlation of sand with Cr (r = -0.373) and Pb (r = -0.174) indicate that these elements can be easily released by ion exchange processes due to the electrostatic interaction of trace metals as they are weakly bound and is bioavailable to the liquid phase (Fostner and Wittman, 1979; Morillo et al., 2004).

Principle component analysis

Principle component analysis has been applied to determine the degree of pollution by metals from lithogenic and anthropogenic sources. The results of PCA for heavy metal contents are listed in Table 6 and Figure 6. Four principal components were extracted, which covered 93.09% of the total variance. Apparently the result of PCA corresponds well with the correlation coefficients. The first component (PC1), with a variance of 50.609%, was highly correlated with Cd, Co, Cu, Ni, Zn and $CaCO_3$; correlation coefficients among this group of elements exceed 0.7 (0.849, 0.878, 0.889, 0.883, 0.910, and 0.951, respectively). The second component (PC2) explained 18.68% of the total variance with significant loadings on Cr and Pb (0.743 and 0.944 respectively), which suggests similar sources. The third component (PC3) explained 13.19% of the total variance with a moderate positive loading on Mn (0.636), suggesting that the sources of Mn could be both natural and anthropogenic. The fourth component (PC4) explained 10.61% of the total variance with a strong positive loading on Fe (0.971). Iron displays none of strong correlations between the other metals, suggesting a different behavior for this element (Hu et al., 2013).

Cluster analysis

Cluster analysis was performed on the same data as PCA to understand the similarities among them. Fig. 7 depicts a dendrogram with single linkage Euclidean and correlation coefficient distance. The cluster analysis results indicate four clusters: (1) Cd-Co-Cu-Ni-Zn-Mn-$CaCO_3$-OM; (2) Sand (3) Fe (4) Cr-Pb in terms of similarities. This indicates that Cd, Co, Cu, Ni, Zn and Mn appear to have originated mainly from same sources. Cluster 2 further shows that sand has no association with these elements. Cluster 3 further shows that Fe has no association with these elements. In addition, Cluster 4 shows that Pb and Cr seem to drive partly from the same sources. This is consistent with our PCA results.

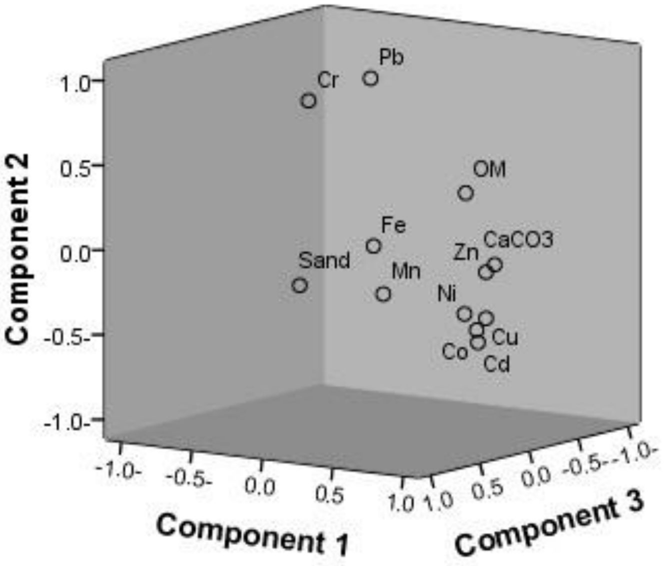

Figure 6: Loading plot of heavy metals in the space defined by PC1, PC2 and PC3

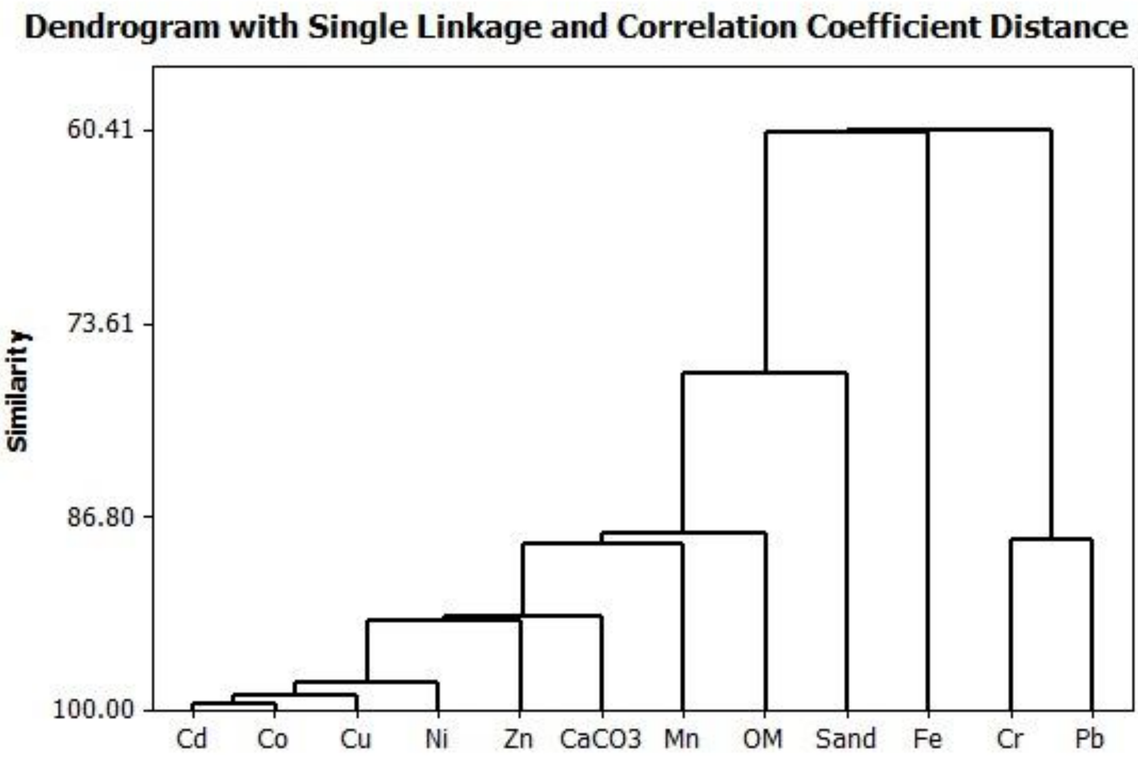

Figure 7: Dendrogram showing cluster of variables on the basic of similarity

Table 5. Correlation Matrix of heavy metal concentrations grain size, carbonate and Organic matter content in Libyan coast zone sediments (No = 14)

	Cd	Cr	Co	Cu	Fe	Mn	Ni	Pb	Zn	$CaCO_3$	OM	Sand
Cd	1											
Cr	-0.891**	1										
Co	0.991**	-0.853**	1									
Cu	0.961**	-0.800**	0.978**	1								
Fe	0.029	-0.150	0.038	-0.025	1							
Mn	0.586*	-0.506	0.619	0.534*	-0.236	1						
Ni	0.937**	-0.795**	0.961**	0.916**	0.021	0.773**	1					
Pb	-0.506*	0.766**	-0.420	-0.352	0.019	-0.291	-0.353	1				
Zn	0.813**	-0.573*	0.830**	0.825**	-0.231	0.713**	0.877**	-0.195	1			
$CaCO_3$	0.830*	-0.603*	0.866**	0.853**	0.211	0.531*	0.871**	-0.108	0.832**	1		
OM	0.473	-0.285	0.520	0.541*	0.164	0.368	0.599*	0.208	0.675	0.759*	1	
Sand	0.328	-0.373	0.376	0.325	0.109	0.541*	0.431	-0.174	0.220	0.266	0.261	1

Table 6: Factor loadings on elements in surfacial sediments samples along the Libyan Mediterranean coastal area (n=14)

Element	PC1	PC2	PC3	PC4
Cd	0.849	-0.487	0.141	0.001
Cr	-0.595	0.743	-0.206	-0.129
Co	0.878	-0.403	0.195	0.006
Cu	0.889	-0.345	0.117	-0.029
Fe	0.035	-0.016	0.035	0.971
Mn	0.524	-0.164	0.636	-0.374
Ni	0.883	-0.289	0.326	-0.050
Pb	-0.077	0.944	-0.094	0.045
Zn	0.910	-0.065	0.146	-0.304
$CaCO_3$	0.951	-0.021	0.117	0.171
OM	0.787	0.394	0.177	0.177
Sand	0.144	-0.106	0.939	0.126
Eigenvalue	6.073	2.242	1.583	1.273
% variance explained	50.609	18.681	13.194	10.610
Cumulative % variance	50.609	69.290	82.483	93.093

Extraction method: Principal component analysis

2. Rotation method: Varimax with Kaiser Normalization

4. CONCLUSION

This work provides the first comprehensive analysis of metal status in surface sediments of the Libyan Mediterranean coast. In this study, three different indices have been employed for the evaluation of heavy metal contamination status in the Libyan Mediterranean Sea. The results showed that total heavy metal concentrations in the sediments samples followed the order: Fe>Pb>Mn>Ni>Zn>Cr>Cu>Co>Cd. According to Muller’s scale, the mean geo-accumulation indexes of Cr, Co, Cu, Fe, Mn, Ni, and Zn are less than zero (Igeo<0), suggesting that the Libyan Mediterranean Sea has not been polluted overall by these metals. On the other hand, the sediment has been strongly to very strongly polluted with Cd (4≤Igeo≤5). This was supported by CF (>6) for Cd. According to the mean PLI value (0.42), the Libyan Mediterranean coast was unpolluted. The heavy metal concentrations in assessed sediment samples were compared with (TEL-PEL) values. The results indicate that Cr and Zn would rarely be expected to cause adverse effects on biota. 79% percent of sediments would be expected to occasionally be associated with the toxic adverse effects on aquatic organisms because of Pb. While, cadmium exceeded the PEL value at 100% of the sediment samples. Multivariate analysis (PCA/CA) and correlation matrix were used in this study. A significant positive correlation is observed among Cd, Co, Cu, Mn, Ni and Zn, indicating that these metals were derived from similar sources. Iron has no association with other elements, suggesting that Fe has another different sources or pathways. The study point out that although there were slight variations in the results of the three indices, the combination of the three indices gave us a comprehensive understanding of heavy metal risks in the surface sediments of the Libyan Mediterranean coast.

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