

Partitioning of Trace Metals in Sediments from the Mediterranean Coastal Zone of Ajdabia to Benghazi, Libya: Case Study

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Abstract

Surface sediment samples were collected from different sites along the Libyan coasts of the Mediterranean Sea from Ajdabia to Benghazi during the period January – April 2012. Collected samples were sequentially extracted using modified BCR procedure and analyzed by FAAS for Cd, Cu, Pb, Fe, Co, Ni, Mn, Zn and Cr. Average total concentrations were 4.49, 5.57, 68.24, 690.40, 17.44, 29.01, 57.97, 32.00 and 18.84 mg/kg for Cd, Cu, Pb, Fe, Co, Ni, Mn, Zn and Cr, respectively. Enrichment factor calculations indicated that Mn, Fe and Cu didn't show any enrichment, while Cr and Zn showed minor enrichment. High enrichments were observed for Cd, Pb, Ni and Co. The results of sequential extraction showed that significant fractions of Cd, Ni, Cr, Pb, Co, and Cu were present in the exchangeable/carbonate phase (20% - 35%). Fe was mainly contained in the residual fraction (58%), while Mn was mainly contained in the Fe-Mn oxide phase. Cu and Zn were predominantly contained in the organic phase followed by the Fe-Mn oxide phase. Co, Ni, Cr and Pb were mainly contained in the Fe-Mn oxide phase (32% - 41%).

Keywords: *Mediterranean Sea; Sediment samples; Sequential extraction; Heavy metals, Enrichment factors.*

Introduction

Heavy metals in marine sediments have natural and anthropogenic origins. The distribution and accumulation are influenced by sediment texture, mineralogical composition, absorption and desorption processes and physical transport. Metals can be absorbed from water onto fine particular surfaces and move toward sediments.^[1] The pollution levels of the aquatic environment by heavy metals can be estimated by analyzing water, sediments and marine organisms. Heavy metals differ from other toxic chemicals in that they are conserved and not degraded in the environment. In nature, they are present as stable minerals such as sulfides, oxides and silicates. These stable minerals are insoluble in water and difficult to breakdown by weathering.^[2,3]

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Marine sediments are considered as a sink for heavy metals. Therefore, understanding the distribution of heavy metals in aquatic systems is of particular importance due to their harmful effects and high toxicity to many aquatic organisms. Several studies have been reported in the literature about the levels, fate and chemical forms of heavy metals in the marine environment of the Mediterranean. Most of these studies were carried out on the European coasts of the Mediterranean. Levels of some elements in Mediterranean coastal regions such as Turkey,^[4,5] Italy,^[6] and France^[7] were reported. On the other hand, few studies were reported about the African coasts of the Mediterranean; Egypt^[8] and Algeria.^[9]

In this study, sediments from Ajdabia to Benghazi in the eastern part of Libya were collected and analyzed by Flame Atomic Absorption Spectrophotometry (FAAS) for Cd, Cu, Pb, Fe, Co, Ni, Mn, Zn and Cr. The primary objectives of the current study were: (1) to determine the average concentrations of some heavy metals in the marine sediment samples collected from different sites along the Libyan coasts of the Mediterranean Sea, (2) to ascertain their mobility and hence bioavailability by using the BCR (Community Bureau of Reference) sequential extraction procedure and (3) to explore the natural and anthropogenic input of heavy metals by correlating their levels to human activities.

Experimental

Study site and sampling

Surface coastal marine sediments from different sites along the Libyan coasts of the Mediterranean Sea from Ajdabia to Benghazi were collected during January – April 2012. A map of Libya indicating the study area is given in Figure 1. Sampling sites were selected to represent different activities along the coast. First set of samples is collected from different locations around one of the major ports mainly devoted to deal with the crude oil and petroleum products. The second set of samples is collected around a power generation and desalination stations powered by gas. The third set of samples is collected from three different common fishing sites. Finally, the fourth set is collected from different locations that are specified for tourism activities.

Twenty four samples were collected from the top 20 cm of the sea sediment at the above mentioned sites. After collection, the samples were directly packed in plastic bags, sealed, labeled, and sent to the laboratory where all samples were dried for 48 hours at about 85 °C in a clean oven, ground, homogenized and sieved through 200 µm sieves.^[10]

Sample Preparation

A modified BCR sequential extraction procedure was used throughout this work. Trace elements were extracted from supposed phases of soil using different solvents. The sequential extraction scheme used in this study is described in Table 1. The

procedure described by Pueyo^[11] was followed to digest the residual fraction from step 3 with some modifications.^[10,12-13]

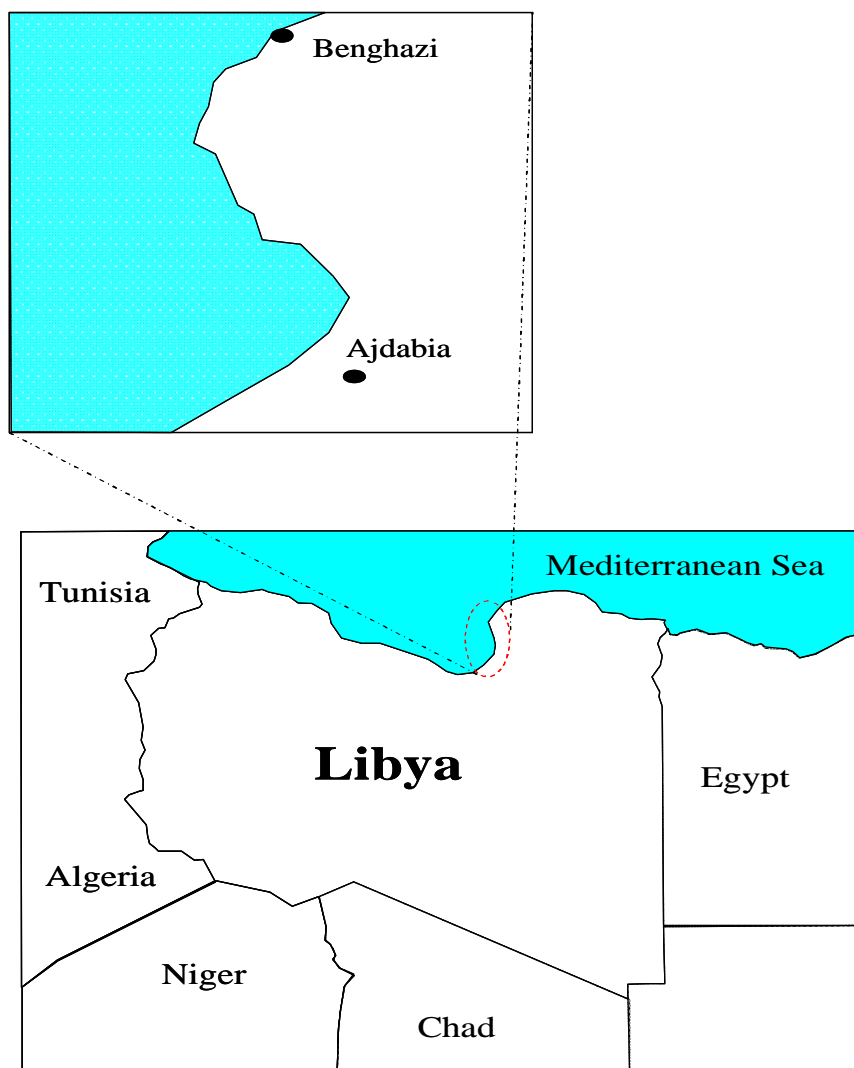


Figure 1: Map of the Mediterranean Coastal Zone of the sampling sites in Benghazi and Ajdabia.

Analysis of the samples

The concentrations of Pb, Cd, Cu, Zn, Co, Ni, Cr, Fe and Mn were determined in all samples using FAAS (Varian Spectra AA, AUSTRALIA). For each element, the measurements were made using its specific hollow cathode lamp. A stock solution, 1000 ppm (BDH chemicals Ltd, Poole, England), was used to prepare the working standard solutions for each element. Recommended procedures described by manufacturers were followed throughout this work.

The detection limits (DL) of the methods were estimated as the concentration that produces three times the standard deviation at the respective wavelengths selected for each element during calibration runs. The detection limits were 6.0, 24.0, 23.0, 4.0, 7.0, 38.0, 6.0, 6.0 and 72 $\mu\text{g/L}$ for Cu, Ni, Zn, Mn, Co, Pb, Cd, Cr and Fe, respectively.^[10]

Table 1: Modified BCR sequential extraction procedure used in this study.

Step	Solid phase	Extraction procedures
F1	Water and weak-acid soluble and exchangeable	1 g of soil sample, 40 mL of 0.11 M CH ₃ COOH, shake (30 ± 10 rpm) for 16 h at 22 ± 5 °C.
F2	Reducible (bound to Fe-Mn oxides)	40 mL of 0.5 M HONH ₂ .HCl (pH 1.5), shake 16 h, room temperature.
F3	Oxidizable (bound to organic sulfides)	10 mL of 8.8 M H ₂ O ₂ (pH 2), shake 1 h, room temperature and 1 h at 85 °C. Then 10 mL of 8.8 M H ₂ O ₂ (pH 2), shake 1 h at 85°C, cool, add 50 mL of 1 M NH ₄ OAc (pH 2), shake 16 h at room temperature.
F4	Residual	10 mL of aqua regia (3:1 HCl/HNO ₃), set overnight at 25 °C, refluxed (the beaker is covered) for about 6 hours then evaporated (the beaker is open) to about 3 mL. Add 4 mL of conc. HF and reflux for 2 hours, then re-evaporated to near dryness. Add 2 mL conc. HNO ₃ , evaporate to about 1 mL then dilute to 50 mL with DD-H ₂ O.

* Steps 1–3 are based on the original BCR protocol.
* Step 4 as described is not standardized in the original BCR procedure; it is based on the procedure described by Pueyo et al.^[11]

Quality Control and Quality Assurance

Blank measurements play a crucial role in the analysis of real samples. Contamination by metals is a strong possibility due to their wide spread distribution. Frequent analysis of blank is the only way to detect and correct any contamination problem. Therefore, blank samples were prepared for each of the extraction steps and during samples digestion. Finally, blank samples were analyzed along with the samples and the average contribution of the added acids and reagents were estimated. All results were blank corrected by subtracting the average blank concentration observed for a certain element from the concentration observed for the same element in each sample. The sample-to-blank ratios for the measured elements were larger than 10. These findings indicate that blank subtraction does not have a significant contribution to the observed concentrations.

The accuracy and precision of the analysis results were checked by periodic analysis of Standard Reference Material (SRM) obtained from the National Institute of Standard and Technology (NIST). Two SRMs were analyzed as samples after being digested using the procedure. Each SRM analysis was repeated three times. The SRMs used in this study are SRM-1646a and SRM-2702. Approximately 0.5 g of the SRM was accurately weighed and transferred into a Teflon beaker and digested using the same microwave digestion procedure and analyzed along with samples. The results for SRMs analysis were in good agreement with the certified values (Table 2).

Table 2: Accuracy and precision based on two SRMs for FAAS analysis (units are in mg/kg except for Fe in %).

Element	SRM-1664a		SRM-2702	
	Found \pm SD	Certified \pm SD	Found \pm SD	Certified \pm SD
Cd	0.13 \pm 0.28	0.15 \pm 0.01	0.84 \pm 0.22	0.82 \pm 0.01
Co	5.26 \pm 0.71	5	25.7 \pm 2.2	27.8 \pm 0.6
Cr	39.6 \pm 1.5	40.9 \pm 1.9	322.2 \pm 5.7	352 \pm 4.7
Cu	9.9 \pm 1.1	10.0 \pm 0.3	94.7 \pm 1.6	
Fe	1.95 \pm 0.19	2.00 \pm 0.04	7.3 \pm 0.48	7.91 \pm 0.24
Mn	232.0 \pm 2.9	234.5 \pm 2.8	1405 \pm 64	1757 \pm 58
Ni	21.5 \pm 2.3	23	76.5 \pm 2.8	75.4 \pm 1.5
Pb	10.3 \pm 4.6	11.7 \pm 1.2	134.6 \pm 2.7	132.8 \pm 1.1
Zn	47.2 \pm 2.9	48.9 \pm 3.6	417.0 \pm 11.4	485.3 \pm 4.2

Results and Discussion

Total concentrations and spatial distributions

The total metal concentration, which is equal to the summation of the concentrations in operationally defined residual and the three non-residual fractions, has been evaluated and presented in Table 3 for each one of the metals of interest. The average concentrations of Cd, Cu, Pb, Fe, Co, Ni, Mn, Zn and Cr were 4.49, 5.57, 68.24, 690.40, 17.44, 29.01, 57.97, 32.00 and 18.84 mg/kg, respectively. The highest average concentration was for iron Fe (690.4 mg/kg) and the lowest was for Cd (4.49 mg/kg).

Figure 2 shows the distribution of measured elements in the coastal sediments of all regions. Except for Zn, the levels of all other measured elements were higher in the sediment samples from the petroleum products port. This finding suggests that most of the pollution in this sampling site is derived from the petroleum products and their industries.

Table 3: Statistical summary for measured elements in collected sediment samples (mg/kg).

Elements	Avg.	SD	Min	Max
Zn	31.98	24.74	12.34	97.22
Mn	58.0	91.3	20.0	482.0
Fe	690.4	710.1	60.0	3901.0
Co	17.44	12.91	0.46	38.96
Cd	4.49	2.18	0.02	8.56
Cu	5.57	4.59	1.45	22.22
Ni	29.01	13.64	6.77	61.74
Pb	68.24	43.92	0.48	169.98
Cr	18.84	11.92	8.08	54.59

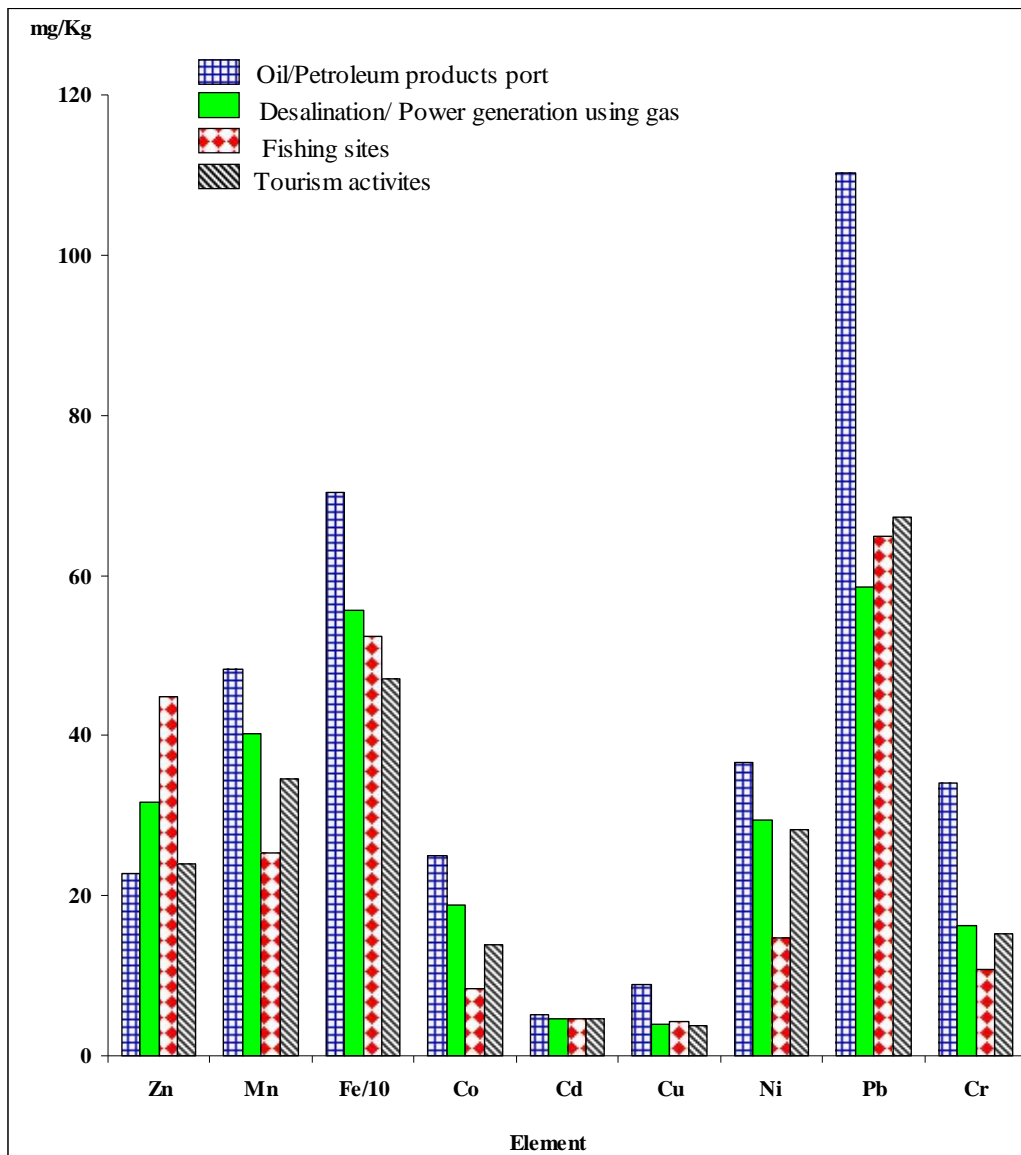


Figure 2: Spatial distribution of measured elements in different coastal sampling sites.

No considerable variations were observed between the measured levels of Cd in the four sub-regions indicating that Cd is equally distributed. Except for the petroleum product port, the levels of Pb and Cu show in the other regions almost a similar trend. The levels of Pb and Cu in the sediments from the petroleum products port were however about two times higher than in those from the other regions. In addition to the high temperature emissions, direct spill of crude oil most likely happens in such huge industrial locations. Actually, we believe that this is the most significant source of pollution in this area. The levels of Pb in sediments collected close to the power generation stations and the desalination stations were the lowest, which might be attributed to the fact that natural gas used in these stations. It is well documented that heavy metals emissions from plants powered by natural gas are much lower than those powered by diesel and coal.^[13]

Maximum levels for Zn were observed in sediment samples collected from the fishing sites, which was 1.5 – 2 times higher than in all other regions. However, fishing sites in general were relatively the cleanest with respect to the remaining elements as compared to the other sites.

Maximum levels for the crustal elements, Fe and Mn, and to a lesser extent Cr, were observed in the petroleum products port sediments followed by the power generation and desalination stations sediments. Lower concentrations and almost equal distribution was observed in the fishing and tourism sites.

Considerable variation in the levels of Co and Ni was observed in the different sampling sites. Highest concentrations were observed in sediment samples collected close to the petroleum products port. As mentioned before, crude oil contains extremely higher levels of heavy metals as compared to all other sources.^[13] Therefore, high temperature emissions and direct spill are believed to be the major sources of heavy metals in this site.

Enrichment Factors

Enrichment factor (EF) was used to interpret and assess the pollution status in sediments from different regions. The enrichment factor model is a double normalization technique used generally to assess the extent of metal contamination compared to the background area.^[14,15] In this study, EF values were calculated using Mn as a reference element and Taylor's compilation^[16] for crustal abundance's according to the following equation:

$$EF = \frac{(C_x / C_{Mn})_{Sample}}{(C_x / C_{Mn})_{Crust}}$$

where $(C_x / C_{Mn})_{soil}$ is the ratio of concentration of the element being determined (C_x) to that of Mn (C_{Mn}) in the soil sample and $(C_x / C_{Mn})_{Crust}$ is the ratio in the reference Earth's crust. An enrichment factor of unity would indicate that the relative concentration of a given metal is identical to that present in unpolluted soil.^[17] However, it is generally accepted to consider EF = 1-5 as not enriched due to the variations in the reference crustal compositions. The most frequently used scale in this context is as follows: EF = 1 to < 5 no enrichment; EF = 5 to < 10 minor enrichment; EF = 10 to < 20 moderate enrichment; EF = 20 to < 50 moderate-high enrichment; EF > 50 high enrichment.^[15,17]

Average and standard deviation of EF values are presented in Table 4. As shown, the EF values for Cu and Fe were less than 5 in all samples from all sites, indicating the absence of any anthropogenic sources affecting the levels of Cu and Fe in the sediment samples. The variability of Fe and Cu in the surface sediments appeared to be controlled mainly by the soil parent materials. Cr and Zn showed minor enrichment in most samples; the EF values ranged between 1-13 for Cr and 2-14 for Zn. These finding reflect the insignificant input of anthropogenic sources. However,

moderate enrichments were observed for samples collected close to the petroleum export port while moderate enrichments were observed for Zn in samples collected close to the fishing sites.

Table 4: Average EF values of measured elements in different sediment samples

	Zn	Mn	Fe	Co	Cd	Cu	Ni	Pb	Cr
Sampling location: Crude oil/petroleum products port									
Avg.	4	1	1.0	29	598	5	22	64	13
SD	2	0	0.0	24	521	4	7	55	9
Sampling location: Desalination and power generation by gas									
Avg.	7	1	1.0	28	716	2	22	45	7
SD	6	0	0.1	12	155	1	7	29	4
Sampling location: Fishing sites									
Avg.	14	1	1.0	18	1043	4	17	74	8
SD	12	0	0.1	15	932	1	7	23	2
Sampling location: Tourism activities									
Avg.	6	1	1.0	22	838	3	25	60	8
SD	3	0	0.0	21	242	1	6	31	5

Moderate to severe enrichments were observed for Ni and Co. The EF values in these samples were in the range 20 to 30. Soil parent materials alone cannot explain these relatively high enrichments for Ni and Co. Cobalt and Ni can be found in many of the same metal products. Due to their chemical properties and their resistance to corrosion, these elements have been widely used for the protection of motor vehicle bodies, fishing tools and oil pumps.^[18]

High enrichments were observed for both Pb and Cd in all samples. This indicates a widespread contamination by Pb and Cd in the coastal sediments. It is well documented that Pb and Cd may have originated from traffic sources. However, direct spill of crude oil does most likely happen in such huge industrial locations. Therefore, the levels of Pb and Cd are extremely influenced by these activities in addition to the automobile exhaust emissions. The high Pb levels are probably contributed to by the deposition of atmospheric Pb emitted from vehicles and industrial point sources which could be carried over very long distances. In addition, Cd, is usually found to be high near roadways due to tire wear.^[19,20]

Heavy metal partitioning in the sediments

Generally, metals are most toxic in the ionic uncomplexed form. Bioavailable fraction can be defined as the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available

or can be made available for uptake by organisms or plants, from either the direct surrounding of the organism or the plant or by ingestion of food.^[21] Chemical contaminants adsorbed to soil particles like metals, have the ability to accumulate in organisms. This accumulation depends on the chemical form that the metals can be found in. In this study, a modified BCR scheme was used to determine the distribution of elements in the different phases.

The partitioning of Pb in all samples is shown in Figure 3. The distribution pattern in each fraction followed the order: Fe-Mn oxides > exchangeable > organic/sulfides phase > residual (silicate). About 28% of the overall Pb is contained in the exchangeable fraction. Lead seems to be equally distributed between the various phases in different samples. In the exchangeable fraction, Pb can be almost completely attributed to anthropogenic sources, and more precisely, to automobile emissions. Lead gasoline has been used for a long period of time. Therefore, the accumulation of Pb with time explains the uniformity of Pb distribution in all samples.^[10]

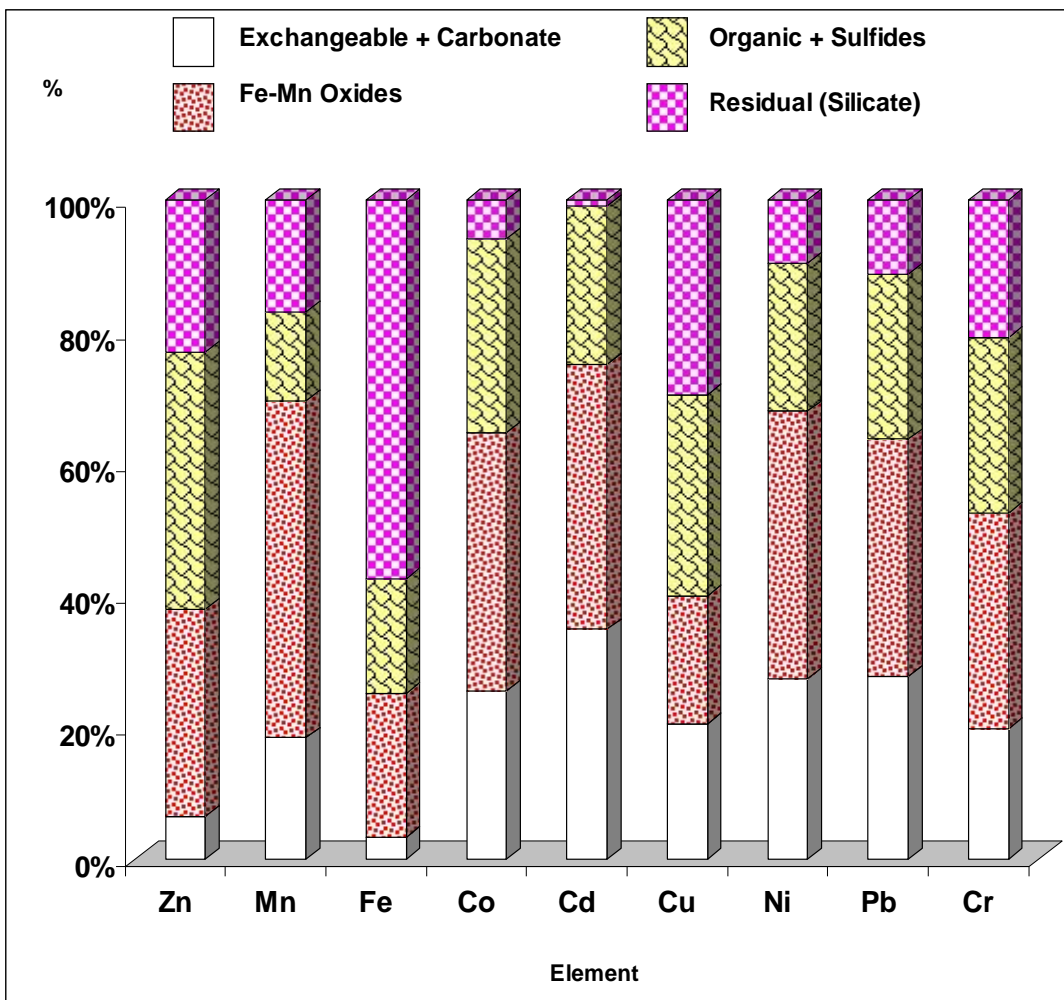


Figure 3: Operationally defined solid phase fractionation (exchangeable + carbonate bound, Fe-Mn oxide bound, Organic bound and residual) for sediment samples from Libyan coasts.

The Cd^{2+} ion adsorb rather weakly on organic matter, silicate clays and oxides unless the pH is greater than 6. Above pH 7, Cd^{2+} can co-precipitate with $CaCO_3$ or

precipitate as pure CdCO_3 .^[22] Large fractions of Cd were found in the exchangeable/carbonate phase. The overall percentage of Cd in the exchangeable/carbonate phase was ~ 35% (Figure 3). These findings are consistent with literature findings.^[23-24] At higher pH the substitution of Cd^{2+} for Ca^{2+} in calcite and the precipitation of CdCO_3 is expected.^[25]

The speciation patterns obtained for Cu in all sediment samples followed the order: organic/sulfides ~ residual > Fe-Mn oxides ~ exchangeable. Large variability in the proportions of Cu present in the organic fraction was observed in samples from different sites. Maximum values were observed for sites characterized by different human activities (tourism sites). However, the organic/sulfides fraction in all coastal sediment samples was the main container for Cu. The presence of Cu in the organic fraction is in strong agreement with what was observed in many earlier studies in soil and sediments.^[26] The presence of Cu in the organic fraction is supported by the high formation constants of Cu–organic complexes. Scanning Electron Microscopy / Energy Dispersive X-Ray (SEM/EDX) analysis on polluted soils confirms also the strong association of Cu with organic matter.^[27] Exchangeable/carbonate fraction accounted for 18-24% of the total Cu. Similar distribution pattern was also observed for Zn. The highest fraction of Zn was tied up in the organic/sulfides phase (40%) followed by the Fe-Mn oxide phase (31%). Exceptionally high fractions of Zn are tied up in the organic/sulfides fraction in samples collected from the tourism sites (~76%) and samples from fishing sites (55%).

The elements Co, Cr and Ni have shown almost similar trends. The distribution pattern for these elements in different fractions was in the order: Fe-Mn oxide > organic phase ~ exchangeable > residual. These findings are in good agreement with those reported by others^[28-30] in which most of the Co, Cr and Ni was found to be tied up in the Fe-Mn oxide phase. The percentage of Co in the exchangeable/carbonate phase varied between 20-30%. However, high fractions of Co were contained in the organic/sulfides phase for samples collected from fishing and tourism sites.^[31] In addition, maximum Co levels are associated with the organic phase in sites that are characterized by the presence of widespread human activities. This explains the increased levels of Co in the organic/sulfides phase in the fishing and tourism sites, 40 and 48%, respectively. However, highest bioavailable fractions for Ni and Cr were found in samples from the petroleum products port.^[10]

Iron was predominantly associated with the residual fraction. Its content in the residual fraction averaged at about 60%. This finding is in good agreement with most of the literature reports.^[32] In unpolluted areas, Al and Fe are always considered as marker elements for crustal contribution. The exchangeable fraction in samples from different categories ranged between 2–6%. Relatively moderate fractions of Fe were associated with the Fe-Mn oxides phase in which the percentages ranged between 20-27% in different samples. However, Mn was associated mainly with the Fe-Mn phase.

The distribution pattern of Mn in different fractions was in the order: Fe-Mn oxide > exchangeable ~ residual > organic/sulfide phase. The same order was also observed for all samples in which the Fe-Mn oxide phase is the predominant one. It is well documented that Mn in crustal unpolluted soil and/or samples is associated mainly with the oxides phase. These findings are in agreement with literature data.^[8]

Conclusions

The present study indicates that the average metal concentrations in sediments of the study area decrease in the order: Fe > Pb > Mn > Zn > Ni > Cr > Co > Cu > Cd. In addition, the distribution of heavy metals in the sediment was not uniform over the study area. In general, highest concentrations were found in sediment samples from the petroleum products port. The results indicate that the levels of Ni and Co are moderately enriched, while Cd and Pb are severely enriched in all samples.

Chemical partitioning of heavy metals in the surface sediments of the Mediterranean Sea showed that significant fractions of Cd, Cu, Pb, Ni and Cu (35%, 26%, 25%, 28%, 27% and 21%, respectively) were contained in the exchangeable/carbonate phase, whereas most of the Fe is contained in the residual (silicates) phase. The Fe-Mn oxides phase tends to hold significant amounts of Mn, Ni, Cd, Cr and Pb. Most of the Cu and Zn appear to be held in the oxidizable organic and sulfide phases.^[10]

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