

Original article

Environmental Pollution Assessment of Some Heavy Metals in Surface Sediments of the Eastern Part of the Coast of Tripoli, Libya

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Abstract

In this study, conducted on sediments from the eastern coast of Tripoli, Libya, in 2025, the aim was to monitor heavy metal pollution in the marine environment. Total organic carbon (TOC) and metals (iron, lead, copper, cadmium, zinc, and manganese) were measured in surface sediments from twelve sites along the eastern coast of Tripoli. Sediments (<63 μm) were analyzed using grain size analysis, the Godet TOC method, and atomic absorption spectroscopy (AAS) after acid digestion. Results showed that the sediments were sandy at most sites (89.61–100%), with a very low clay content (<0.35%) and varying silt content (0–10.39%). Sites S4, S6, and S8 were purely sandy, while the silt content was higher at sites S9 and S11. Total organic carbon (TOC) ranged from 0.023 to 0.079%, with the highest values recorded in fine sediments, indicating a direct link between silt and organic matter. Heavy metal analysis results showed spatial variation: iron (207.12–376.41 mg/kg) was highest in Tripoli Port (S1–S3); lead (0.77–4.76 mg/kg) was highest near the port; copper (10.04–48.47 mg/kg) peaked in S1 and S12; cadmium (Cd) rose to 2.35 mg/kg in the port areas, indicating an anthropogenic contribution; zinc (8.95–30.22 mg/kg) and manganese (53.96–117.4 mg/kg) were the opposite. Environmental indicators supported these patterns: the enrichment factor (EF) indicated very high enrichment of cadmium and copper at port sites (S1, S12); the pollution load index (PLI) ranged between 0.25 and 0.83, with the highest level in S1, but all were below 1, indicating the absence of severe pollution; the geological accumulation index (Igeo) showed sediments uncontaminated with iron, lead, zinc, and manganese, while cadmium content ranged from uncontaminated to moderately contaminated. Heavy metal contamination was generally limited, with the exception of localized cadmium and copper concentrations near commercial and fishing ports. The results indicate the impact of human activities on marine sediment quality, with areas near ports and industrial facilities experiencing higher levels of pollution, underscoring the need for continuous monitoring.

Keywords. Eastern Coast of Tripoli, Heavy Metals, Pollution Indices.

Introduction

Marine pollution is one of the most prominent environmental issues that directly impacts marine ecosystems and the organisms that inhabit them. Seas and oceans are exposed to a wide range of pollutants, including chemicals, plastic waste, and heavy metals, which accumulate in surface sediments, affecting the quality and sustainability of the marine environment. Heavy metals are among the most dangerous pollutants due to their ability to bioaccumulate and move through the food chain, leading to negative impacts on human health and marine organisms. These elements include iron, cadmium, copper, lead, zinc, and manganese. Their sources vary from natural sources, such as rock weathering, to human activities, such as industrial discharges, marine waste, oil spills, maritime activity, and fishing. The impact of heavy metals on marine ecosystems extends to physiological and behavioral changes in organisms, as high levels can cause cellular toxicity, metabolic disturbances, and impact the reproductive and growth processes of many marine organisms. The accumulation of these elements in surface sediments disrupts the ecological balance of the seabed, affecting biodiversity and the stability of marine communities. Elevated metal levels in aquatic ecosystems raise global environmental and health concerns [1].

The risk of these contaminants being resuspended in the water column as a result of hydrodynamic activities increases, further enhancing their negative impacts on the ecosystem. Metals constitute a major group of aquatic pollutants and are of particular importance in the field of ecotoxicology due to their high persistence, as well as their non-biodegradability and bioaccumulation properties [2]. The importance of this research in studying the impact of heavy metal pollution on the marine environment is highlighted by understanding the prevalence of these elements in surface sediments, the factors controlling their accumulation, and their environmental impacts. This helps assess potential risks to public health and the environment, particularly in coastal areas experiencing intense marine and industrial activity.

Rapid industrialization and uncontrolled urban expansion around many Libyan cities and coastal areas have led to alarming levels of metal pollution in the aquatic environment, where metals contain high enrichment factors and slow removal rates [3]. This study also contributes to filling research gaps related to the lack of data on surface sediment pollution in the eastern coastal region of Tripoli, as insufficient studies have been conducted to assess the impact of human and industrial activity on heavy metal concentrations in this region. This study aims to determine the concentrations of heavy elements, including iron, cadmium, copper, lead, zinc, and manganese, in the surface sediments of the study area by analyzing samples taken from various locations within the eastern coastal region of Tripoli. This area

is characterized by the presence of the main port, Tripoli, in addition to several smaller ports and fishing harbors, making it vulnerable to heavy metal pollution. The study also aims to assess the relationship between measured concentrations and potential sources of these pollutants, whether resulting from maritime or industrial activity, and to compare pollution levels with international environmental standards to determine the severity of pollution in the region.

Several previous studies have assessed heavy metal pollution in the southern and eastern Mediterranean, as well as along the Libyan coast. These studies have shown that coastal areas near ports and industrial areas suffer from significant accumulation of heavy metals in surface sediments. Sediment pollution assessment procedures using calculated indices, such as the pollution factor (CF), enrichment factor (EF), modified pollution degree (mCd), pollution load index (PLI), and geoaccumulation index (Igeo), are widely applied to assess the status of metal pollution and sediment enrichment [1,4,5]. These indicators are considered sensitive indicators of the impact of various human activities on aquatic ecosystems [4,6].

The current study relies on the application of several international indicators to assess the level of heavy metal pollution in the surface sediments of the study area, including the Environmental Enrichment Index (EF), the Pollution Load Index (PLI), and the Geoaccumulation Index (Igeo). These indicators help determine the extent to which the area is affected by pollution and determine whether its source is natural or human-caused. This assessment contributes to providing an accurate and comprehensive analysis of the pollution situation in the eastern coastal area of Tripoli, which is witnessing a population increase and the expansion of marine activities. This reinforces the need to assess the impact of these factors on the quality of the marine environment and surface sediments, and to take appropriate measures to protect the marine ecosystem from potential environmental risks.

Study boundaries

The study area is located on the eastern coast of Tripoli, Libya, on the Mediterranean Sea. It extends from Tripoli Port at 32°54'44.91"N and 13°12'24.11"E and heads east to beyond the Qaryouli fishing harbor at 32°49'9.93"N and 13°45'48.60"E, a distance of approximately 5.5 km. The region has witnessed significant urban development through a comprehensive waterfront plan that aims to achieve a balance between investment and environmental conservation. It also boasts extensive maritime activity, with Tripoli's seaport, one of the largest in North Africa, receiving thousands of ships and handling millions of tons of cargo annually. Fishing is also a major activity, particularly in ports such as Tajoura Port and Al-Qarbouli Port. Given this intense activity and urban expansion, the region is an ideal location for studying heavy metal pollution. Human activities, such as shipping and urban expansion, can increase pollutants in marine sediments. Furthermore, coastal changes caused by construction and development can affect the distribution and concentration of pollutants, making studying their impact essential to understanding potential environmental risks.

Table 1. Locations and distances of sediment samples taken from the eastern coast of Tripoli (study area)

Site no	Latitude (N)	Longitude (E)	Distance among samples (m)	
S1	N" 44.91'32°54	E" 24.12'13°12	1-2	2900
S2	N" 27.40'32°55	E" 5.69'13°14	2-3	4370
S3	N" 26.39'32°55	E" 50.96'13°16	3-4	4330
S4	N" 2.70'32°55	E" 37.03'13°19	4-5	4420
S5	N" 42.65'32°54	E" 27.94'13°22	5-6	5750
S6	N" 22.41'32°53	E" 50.31'13°25	6-7	7380
S7	N" 17.08'32°51	E" 51.05'13°29	7-8	7110
S8	N" 15.20'32°50	E" 14.84'13°34	8-9	5870
S9	N" 58.99'32°48	E" 42.13'13°37	9-10	5710
S10	N" 8.88'32°49	E" 20.29'13°41	10-11	7000
S11	N" 9.93'32°49	E" 48.60'13°45	11-12	2760
S12	N" 52.28'32°47	E" 57.33'13°44	Beach -12	Nearly 300

Materials and Methods

Sampling Sites

Marine sediment samples weighing approximately 1 kilogram were collected during 2024 from 12 sites covering the target study area (Figure 1 and Table 1). Samples were cut from the center of the catcher using a plastic spoon to avoid metal contamination. They were placed in sealed polyethylene bags, pre-washed with 1:1 hydrochloric acid, and rinsed with metal-free water. Locations were identified using GPS, and sites were selected to cover areas affected by various activities.



Figure 1. The positions of sediment samples in the study area.

Sample preparation

The samples were then dried in the laboratory on plastic plates for several days at room temperature inside a clean cabinet until they reached a constant weight. The samples were then sieved through a 2 mm sieve to remove any gravel. Then each sample was divided into two sub-samples. One subsample was used for grain size analysis, while the other subsample was homogenized using an agate mortar in order to normalize the variation in sediment grain size in the sample, and kept in clean, well-sealed polyethylene containers until analysis.

Grain size analysis

About (18-32 g) of dried samples was taken for mechanical analysis. The samples were subjected to the combined technique of dry sieving and pipette analysis according to the method described by [1]. Grain size determination was made on the dried samples by the conventional sieving method. Dry sand was fractionated by dry sieving using sieves with openings of (2, 1, 0.5, 0.25, 0.125, 0.063, and 0.032 mm) and an electric shaker, and the pipette analysis technique was used for separation of sand, silt, and clay fractions to illustrate the sediment types.

Total organic carbon

Total organic carbon (TOC) was determined according to the (Gaudette and Flight) method, which has been used in many similar studies, including Study [1].

Analysis of Sediment Samples

Total concentrations of heavy metals (iron, lead, copper, cadmium, zinc, and manganese) were determined in samples digested in an open system with a mixture of concentrated compounds (HNO₃/HClO₄/HF) at a ratio of (6:3:1) according to the method of [6] which has been followed in many similar studies, including [1].

Table 2. Grain size distribution, total organic carbon, and heavy metals in sediment samples (study area)

Sit no	(%)				Heavy metals $\mu\text{g/g}$						Nomenclature
	Sand	Silt	Clay	TOC	Fe	Pb	Cu	Cd	Zn	Mn	
S1	97.77	2.08	0.15	0.034	376.41	3.631	48.47	2.35	23.6	117.4	Fine sand
S2	98.21	1.41	0.35	0.048	353.81	4.76	37.52	0.9018	30.22	109.31	Medium sand
S3	98.41	1.31	0.28	0.072	322.3	3.327	15.58	0.82	24.06	95.42	Medium sand
S4	100	0	0	0.024	261.2	1.169	10.044	0.373	14.07	71.81	Very Coarse sand
S5	99.69	0.19	0.12	0.057	293.21	0.77	12.17	0.46	11.85	62.78	Very Coarse sand
S6	99.21	0.79	0	0.039	253.7	2.876	10.78	0.685	17.47	78.63	Medium sand
S7	99.8	0	0.2	0.023	215.11	2.97	19.85	0.6957	15.45	53.96	Very Coarse sand
S8	99.78	0.22	0	0.031	207.12	2.05	14.04	0.284	25.21	91.36	Very Coarse sand
S9	89.61	10.39	0	0.079	221.31	1.231	11.09	0.732	19.38	ND	Fine sand
S10	95.98	4.02	0	0.062	273.63	3.102	34.85	0.9621	10.69	98.24	Fine sand
S11	91.76	8.2	0.08	0.072	267.21	1.72	18.03	0.772	8.95	73.55	Fine sand
S12	96.09	3.91	0	0.07	308.44	3.17	41.71	2.01	22.02	102.11	Fine sand

Results and Discussion

Grain size analysis

The data in Table 2 show that the surface sediments in the study area are mostly composed of sand, with a very high percentage ranging between 89.61% and 100%. This indicates the dominance of coarse and medium sand sediments in most sites. Site S4 showed the highest sand percentage (100%), with no silt or clay, indicating exposure to strong water currents or active marine dynamics that prevent the deposition

of fine materials. The same applies to a large extent to sites such as S7, S8, S5, and S6, where the sand percentage exceeded 99%. Silt ranged between 0% and 10.39%. Site S9 was the most exceptional, recording the highest silt percentage (10.39%) and the lowest sand percentage (89.61%) compared to the other sites. Relatively high percentages of silt were recorded at sites S11 and S10, at 8.2% and 4.02%, respectively. Clay, on the other hand, was very low at all sites, not exceeding 0.35%, and was completely absent at several sites (S4, S6, S8, S9, S10, and S12), reinforcing the hypothesis of high dynamic activity in the area that does not allow for the deposition of very fine particles. Overall, these results indicate that the majority of the study sites are located within an active sedimentary environment, predominantly sandy, with limited variation in silt percentages and a scarcity of clay, which is often attributed to the influence of strong ocean currents or disturbances associated with human activity, such as maritime navigation or bottom dredging.

Total organic carbon (TOC%)

The results shown in Table 2 show that the total organic matter (TOC) concentration ranged between 0.023% and 0.079%, indicating relatively low levels of organic matter at most of the studied sites. The highest value was recorded in S9 (0.079%), while the lowest value was in S7 (0.023%). These low organic matter values are closely related to the sediment composition at the studied sites, as the data indicate that sand constitutes the predominant percentage at most sites, exceeding 95% in 9 out of 12 sites. Meanwhile, sites with higher silt content (S9, S10, S11, and S12) tended to record higher TOC values.

Figure 2 shows a linear relationship between the silt percentage (%) and the total organic content (%), with a downward slope. It is clear from the graph that there is a direct relationship, with the TOC value increasing with the increase in the silt content in the sample. This is clearly evident at sites such as S9, S11, and S12, which recorded the highest silt content and highest TOC levels.

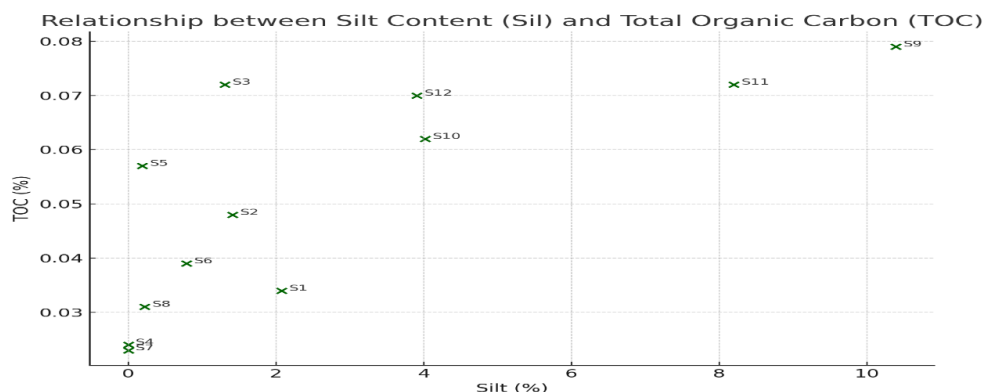


Figure 2. The graph shows the linear relationship between (Silt%) and (TOC%), with a regression line

This supports the hypothesis that fine sediments facilitate the accumulation of organic matter. These observations are consistent with what was reported by [5] and are included in many studies, including [7], which indicated that organic matter increases with decreasing grain size, as silt protects organic matter from decomposition and provides a larger surface area for the stabilization of organic compounds and minerals. Adesuyi [8] also indicated that fine-grained sediments provide greater opportunities for the accumulation of pollutants due to their physical and chemical properties. Thus, total organic carbon (TOC) is a good indicator for understanding the capacity of sediments to absorb pollutants, particularly heavy metals, which are often associated with organic matter in the marine environment.

Heavy metal concentration

Heavy metals were analyzed according to the method of (Oregioni and Aston), referred to in reference [9], where approximately 0.2 g of each sample was placed in a digestion tube, and 10 ml of a mixture of three acids, hydrofluoric acid, nitric acid, and perchloric acid, was added to it in a ratio of (1:4:6), and left at room temperature for an hour. The digestion tubes were placed in a water bath for 3 hours. After that, the samples were cooled in the laboratory atmosphere and the volume was completed to 25 ml with 1N-HCl. Then the samples were filtered. If some samples were not fully digested, 10 mL of 1N-HCl was added and left in a water bath for three hours again. The first process was repeated, and the digested samples were filtered and ready for analysis. The control solution is prepared by placing 10 mL of the mixture of the three primary acids, then heating it in a water bath for 3 hours, cooling it, and completing the volume to 25 mL of 1N-HCl. Calculated from the following equation: concentration ($\mu\text{g l}^{-1}$) = (25/W) x $\mu\text{g ml}^{-1}$. By Atomic Absorption Spectroscopy (AAS).

Table 2 shows the values obtained for the percentage of total organic carbon and the analysis of heavy elements (Iron, lead, Copper, Cadmium, Zinc, and Manganese) using the Atomic Absorption Spectrophotometer (AAS) Shimadzu 6800.

Iron

The distribution of iron (Fe) was studied, and the results showed a clear variation in iron concentration and organic content between samples. The highest iron concentration was recorded in sample S1, taken from Tripoli Seaport, at 376.41 mg/kg. This increase is attributed to commercial and maritime activity. Relatively high levels were also recorded in samples S2 and S3, located closer to the port, where concentrations reached 353.81 mg/kg and 322.3 mg/kg, respectively, reflecting a clear decreasing effect of metal pollution with distance from its main source.

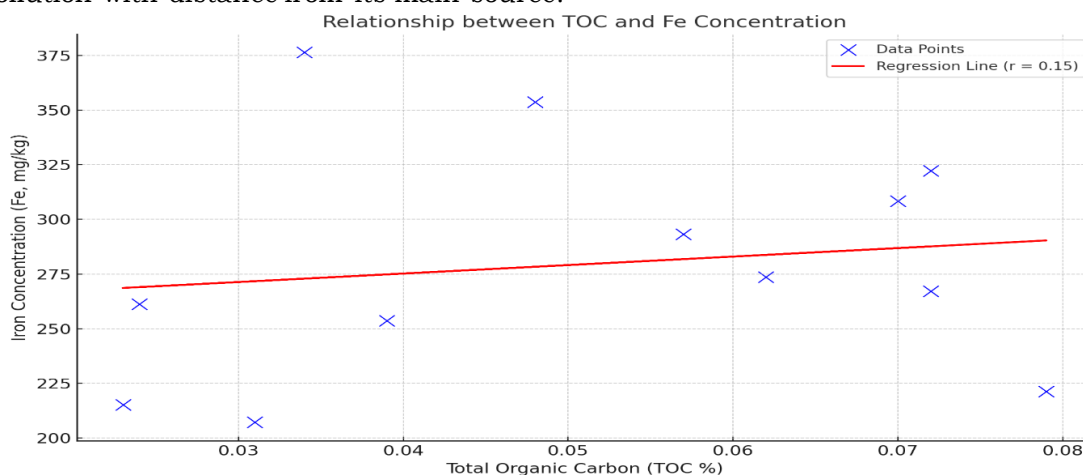


Figure 3. The (TOC) and iron (Fe) in sediment samples

In sample S5, located near Tajoura Fishing Port, the iron concentration reached 293.21 mg/kg, with an organic content of 0.057%. These values indicate moderate pollution. While sample 12 (S12), taken from a small fishing port in Qarbouli, showed a relatively high iron concentration (308.44 mg/kg) and a high organic content (0.07%), suggesting the possibility of local sources of pollution, such as domestic wastewater or fishing waste. The remaining samples, particularly S6 to S11, showed relatively low iron levels, with S7 and S8 recording the lowest values (215.11 and 207.12 mg/kg, respectively), along with low organic content. and the red line represents the linear regression equation between them. The results indicate a relative relationship between high iron concentrations and increased organic content at some sites. In general, the iron oxidation pathway is affected by many factors (such as pH and temperature) [7]. The results obtained in this study were almost consistent with the study of (Al-Dhuwaib et al., 2019) on the sediments of the Mediterranean Sea off the Libyan coast, which ranged between (230-704 $\mu\text{g/g}$), and to some extent with the study of [8] in the Zawiya oil port, which ranged between (975: 2771 with an average of 1612 $\mu\text{g/g}$) for iron. There was a slight and approximate difference with the study of [9] on the western coast of Tripoli, which ranged between (202.42-347.21 $\mu\text{g/g}$). The maximum concentration of total iron is less than 10% of what was recorded in the sediments of the eastern port (3,351.8 mg/kg-1; [9]). This is much lower than that recorded in Damietta Port sediments, which ranged between (14216-55619 ppm [10,8]), and that recorded in northwestern Spain sediments (22970 mg/kg-1; [11]). The figure shows the relationship between TOC and Fe. The correlation coefficient $r \approx 0.65$ indicates a moderate direct relationship between TOC and Fe concentration.

Lead

The results for lead (Pb) and total organic carbon (TOC) concentrations in sediment samples from twelve different sites in the study area showed significant spatial variation. The highest lead concentration was recorded at site S2 (4.76 mg/kg), followed by S1 (3.63 mg/kg) and S3 (3.33 mg/kg). All of these sites are located near active marine areas (Tripoli Harbor) and likely reflect pollution from this area. These high lead levels were accompanied by moderate TOC values. Site S12 also showed a relatively high lead level (3.17 mg/kg) with a high TOC (0.07%), suggesting the presence of local pollution sources rich in organic matter, such as fishing waste or sewage discharge. Similarly, site S10 showed high levels of both lead (3.10 mg/kg) and TOC (0.062%). In contrast, site S5 recorded the lowest lead concentration (0.77 mg/kg) despite an average TOC concentration (0.057%). Other sites, such as S4 and S9, showed low lead levels (1.17 and 1.23 mg/kg, respectively), although S9 had the highest TOC content (0.079%) among all samples. The overall relationship between TOC and lead appears weak, as confirmed by the low correlation coefficient ($r \approx 0.09$).

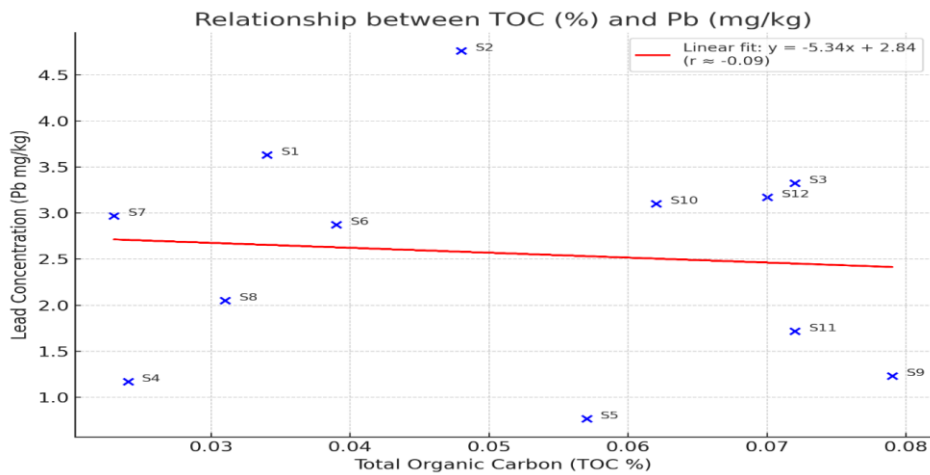


Fig 4. The (TOC%) and (Pb, mg/kg) in sediment samples

This suggests that organic content alone does not control lead distribution and that other environmental factors, such as sediment composition, pH, and hydrodynamics, may play a more dominant role. The graph in Figure 4 is a scatterplot illustrating the relationship between total organic carbon (TOC%) and lead concentrations (Pb, mg/kg) in sediment samples. The red line represents the linear regression, indicating a weak negative correlation.

Copper

Results of copper (Cu) and total organic carbon (TOC) concentrations in sediment samples taken from twelve different sites in the study area showed significant spatial variation. The highest copper concentration was recorded at site S1 (48.47 mg/kg), followed by site S12 (41.71 mg/kg), and then site S2 (37.52 mg/kg). All of these sites are located near the port of Tripoli, indicating a potential influence of human activities, including ship traffic, industrial discharge, and urban runoff. These high copper concentrations were generally associated with low to moderate TOC levels (0.034% at site S1, 0.07% at site S12, and 0.048% at site S2). Site S10 also showed a high copper concentration (34.85 mg/kg) along with a relatively high TOC content (0.062%), which may indicate local inputs of organic-rich pollution, such as sewage or organic waste discharge. Conversely, site S4 recorded one of the lowest copper concentrations (10.044 mg/kg) with a very low TOC value (0.024%). Similarly, low copper levels were observed at sites S6 (10.78 mg/kg) and S9 (11.09 mg/kg), although site S9 had the highest TOC content (0.079%) among all samples. Interestingly, site S5 showed a low copper concentration (12.17 mg/kg) despite a moderate TOC value (0.057%), suggesting that organic matter is not the only factor influencing copper distribution. In general, the correlation between TOC and copper appears weak, as visually demonstrated in the scatterplot in Figure 5, where the linear regression line indicates a negligible correlation. Figure 5 is a scatterplot illustrating the relationship between TOC% and copper concentrations (Cu, mg/kg) in sediment samples. The red line represents the linear regression, indicating a weak correlation.

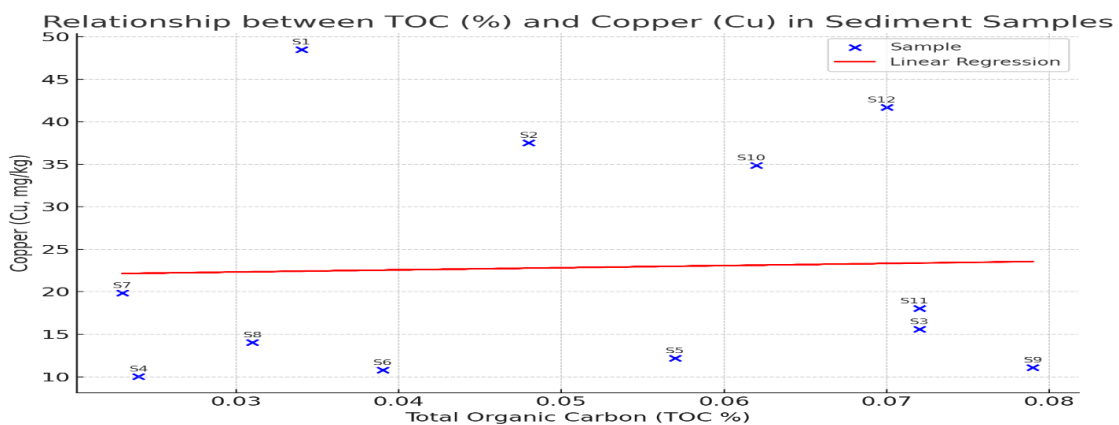


Fig 5. The (TOC%) and (Cu, mg/kg) in sediment samples

Cadmium

The results showed significant variation in cadmium concentrations between samples. The highest concentration was recorded at Site 1, at 2.35 mg/kg, followed closely by Site 12, at 2.01 mg/kg. These high levels may be related to human activities. Site 1 is located in a busy commercial port, which could

explain the high level of contamination. Site 12 may also be affected by similar anthropogenic sources. In contrast, the lowest cadmium concentration was recorded at Site 8 (0.284 mg/kg), a site presumably far from major pollution sources. Most other sites, such as S4, S5, S6, S7, and S9, showed moderate cadmium levels between 0.3 and 0.9 mg/kg, levels considered within or slightly above natural background levels for coastal sediments. For total organic carbon (TOC), values ranged from 0.023% (S7) to 0.079% (S9). Interestingly, the sites with the highest TOC content (such as S3, S9, S11, and S12) did not always correspond to the highest cadmium levels. Site 3 recorded a TOC of 0.072%, with a relatively low cadmium concentration of 0.82 mg/kg, while Site 12, which had a similar TOC (0.07%), showed a much higher cadmium level (2.01 mg/kg).

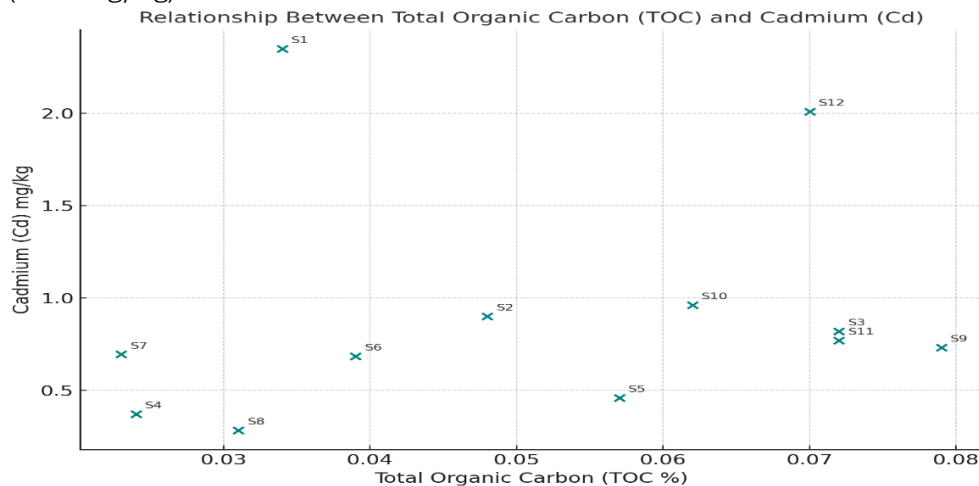


Fig 6. The (TOC%) and (Cd) concentrations in surface sediments

From the graph in Figure 6, it is clear that there is no clear linear relationship between total organic carbon (TOC) and cadmium in this data set. The data indicate that site-specific factors, such as proximity to pollution sources and human activities, are likely the most influential factors on cadmium levels, not organic matter.

Zinc

Zinc (Zn) and total organic carbon (TOC) concentrations in sediment samples collected from twelve different sites in the study area showed clear spatial variation, with the highest zinc concentration recorded at site S2 (30.22 mg/kg), followed by site S8 (25.21 mg/kg), and then site S3 (24.06 mg/kg). Medium to low levels of TOC were also recorded (0.048% at site S2, 0.031% at site S8, and 0.072% at site S3), indicating that high zinc levels are not necessarily associated with high organic content. Site S1 also showed a relatively high zinc concentration (23.6 mg/kg) with low TOC (0.034%), due to the presence of external zinc inputs from ship and barge traffic in Tripoli Port (maritime activities). The lowest zinc concentrations were observed at site S11 (8.95 mg/kg) and site S10 (10.69 mg/kg), both of which recorded relatively high TOC values (0.072% in S11 and 0.062% in S10). This pattern suggests a possible dilution effect or reduced zinc availability in organic-rich environments. Site S5, despite its moderate TOC level (0.057%), showed low zinc levels (11.85 mg/kg), confirming that TOC alone does not control zinc distribution. Notably, site S4 recorded a zinc concentration of 14.07 mg/kg, one of the lowest TOC values (0.024%), and site S7 recorded similar values (15.45 mg/kg zinc and 0.023% TOC), indicating low zinc and organic matter content in these areas, possibly due to limited human influence.

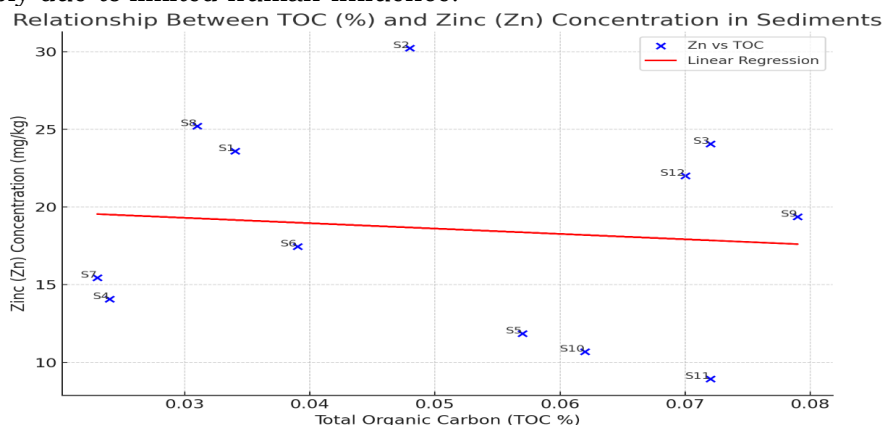


Fig 7. The (TOC%) and (Zn) in sediment samples from the study area

In Figure 7, the scatterplot shows the relationship between total organic carbon (TOC%) and zinc (Zn) concentration (mg/kg) in sediment samples in the study area. Each point is labeled with its location

number. The red line represents the linear regression, indicating a weak negative correlation between TOC and Zn concentration. This illustration supports the previous interpretation: TOC does not appear to strongly influence the distribution of zinc in sediments, suggesting that other environmental or human factors may be more important.

Magnesium

Results of manganese (Mn) and total organic carbon (TOC) concentrations in sediment samples collected from twelve sites show significant spatial variation. The highest Mn concentration was recorded at site S1 (117.4 mg/kg), followed by site S2 (109.31 mg/kg), and then S12 (102.11 mg/kg). These three sites are located in or near Tripoli Harbor, indicating a significant influence of ship traffic and marine activities. Despite these relatively high manganese values, TOC levels were low to moderate (0.034% at site S1, 0.048% at site S2, and 0.07% at site S12). Site S3 also recorded a relatively high manganese concentration (95.42 mg/kg) with a TOC of 0.072%, while site S10 showed a concentration of 98.24 mg/kg of manganese and 0.062% TOC, which may reflect local organic inputs or sediment characteristics favorable for manganese retention. In contrast, low manganese concentrations were recorded at S7 (53.96 mg/kg) and S5 (62.78 mg/kg), despite moderate TOC values (0.023% and 0.057%, respectively). Manganese concentrations were not detected in S9 (ND) despite the highest TOC value (0.079%), highlighting the lack of a direct correlation.

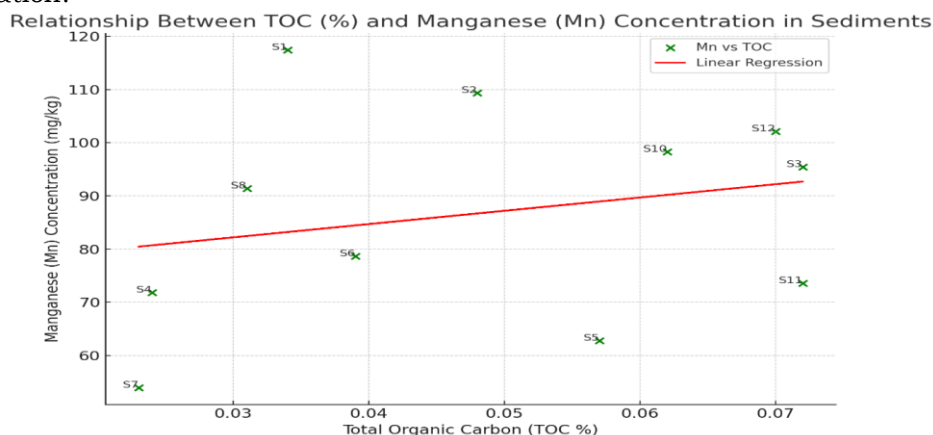


Fig 8. The (TOC%) and (Mn) in sediment samples from the study area

The relationship between TOC and manganese is weak, as shown in the scatterplot in Figure 8. While the linear regression line (in red) indicates a very slight positive trend, the data points are widely scattered, suggesting that manganese distribution is likely influenced by multiple factors beyond TOC content, such as redox conditions, mineralogical properties, and external anthropogenic inputs such as marine activities.

Environmental indicators

In this study, we did not analyze aluminum concentrations in sediments. Instead, iron (Fe) was used to calculate the enrichment factor. Iron is a common element in clay mineral structures and is also associated with particle surfaces as oxide layers. Iron (Fe) in estuarine sediments, however, is primarily a product of natural weathering processes and has been widely used to normalize metal concentrations to reduce the effect of particle grain size [7,10,12]. Therefore, it is considered logical to use iron (Fe) to calculate the metal enrichment factor. In fact, several researchers have successfully used iron to normalize heavy metal contaminants [10,7]. According to [11], the metal enrichment factor (EF) is calculated using the following equation:

$$Ef = \frac{\text{Sample (Metal/Fe)}}{\text{(Metal/Fe) Background Information}}$$

Elements can be divided into three main groups based on their respective enrichment factors: unenriched elements (EF < 10), moderately enriched elements (EF < 100), and highly enriched elements (EF > 100).

Table 3. Calculated enrichment factor and pollution load index for sediment samples on the eastern coast of Tripoli (study area)

Sit no	EF Pb	EF Cu	EF Cd	EF Zn	EF Mn	PLI
S1	26.78	243.12	2,946.78	41.68	17.32	0.85
S2	31.75	200.21	1,203.05	57.59	17.16	0.71
S3	24.36	91.27	1,200.87	50.34	16.44	0.50

S4	10.56	72.60	674.03	36.32	15.27	0.27
S5	6.20	78.36	740.49	27.25	11.89	0.25
S6	26.75	80.22	1,274.42	46.43	17.21	0.40
S7	32.58	174.22	1,526.52	48.43	13.93	0.41
S8	23.36	127.98	647.20	82.07	24.49	0.36
S9	13.13	94.61	1,561.18	59.05	NaN	0.49
S10	26.75	240.46	1,659.58	26.34	19.94	0.52
S11	15.19	127.39	1,363.66	22.58	15.28	0.35
S12	24.25	255.31	3,075.87	48.14	18.38	0.73

Table 3 shows the contamination levels at twelve sites in the study area, based on calculated enrichment factors (EF) for a group of heavy metals: cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), and zinc (Zn), as well as the general pollution load index (PLI). The results showed significant differences in contamination levels between sites, indicating varying degrees of human influence across the region. In S1 and S2, the results showed the highest levels of heavy metal enrichment among all sites. Very high enrichment factors were recorded for cadmium (EF_{Cd} = 2946.79) and copper (EF_{Cu} = 243.12) in S 1, located in Tripoli port, where the general pollution load index was 0.83, while in S 1 2, located in Qarbouli fishing marina, the cadmium (3075.87) and copper (255.31) had a pollution index of 0.73. This indicates a strong and potential pollution source due to the presence of large quantities of pollutants, due to the various marine activities in the port and marina. In contrast, station S 5 showed the lowest pollution levels, where the EF_{Cd} was 740.49, the EF_{Cu} was 78.36, and the pollution index was only 0.25. Similarly, Station 4, with EF_{Cd} of 674.03 and EF_{Cu} of 72.60, recorded the lowest pollution index (EF) in the dataset (0.27), reflecting a relatively clean environment, likely due to the site's distance from major pollution sources.

Station S8, while not recording the highest EF values in this dataset, showed significant enrichment in cadmium (EF_{Cd} = 647.20) and copper (EF_{Cu} = 127.98), with a pollution index (PLI) of 0.36. These results, however, indicate a significant level of pollution, consistent with the expected impact of commercial port activities, such as oil discharge, antifouling coatings, and marine debris. Lead (Pb) and manganese (Mn) showed consistently high EF values at most sites, with EF_{Pb} values ranging from 6.20 to 32.58, and EF_{Mn} values generally exceeding 10. These results may indicate both natural and widespread anthropogenic contributions. The elevated manganese levels, in particular, may reflect geological background sources rather than direct contamination.

Overall, the data demonstrate a strong influence of human activity on sediment quality in the study area, particularly in locations close to active port facilities. The elevated EF values for cadmium and copper at several stations highlight the potential environmental risks posed by the accumulation of metals in marine sediments. Based on these results, it is recommended to strengthen environmental monitoring programs along the eastern coast of Tripoli, particularly in and around commercial and fishing ports. Effective marine litter management, stricter controls on waste disposal, and periodic assessments of sediment and water quality are essential to reduce heavy metal contamination. Further research should also include analysis of surface water and suspended particulate matter to improve tracking of pollution sources and guide targeted treatment strategies.

Pollution Load Index

To investigate the pollution state in the study area, pollution load index (PLI) was computed according, [7] using the following equation:

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n}$$

Where:

PLI = Pollution load index.

CF = Contamination factor, which is equal to the concentration of the metal in the sediment sample divided by its background concentration.

N = number of metals investigated. The following terminologies are used to describe the contamination factor: (CF<1) low contamination factor; (1<CF<3) moderate contamination factor; (3<CF<6) considerable contamination factor, and (CF>6) very high contamination factor [12]. The calculated values of the pollution load index at the study stations indicate a clear variation in the levels of metal pollution in the marine surface sediments in the studied area, as stations S4, S5, S6, S7, S8, S9 and S11 recorded low values of the PLI index ranging between (0.25 - 0.49), indicating that these stations were not exposed to significant metal pollution effects. It is likely that these sites are located in areas far from industrial or urban pollution sources, or that natural processes such as sedimentation and dilution helped in reducing the accumulation of heavy metals in the sediments. On the other hand, stations S3, S10, S2, and S12 showed relatively higher levels of pollution, with PLI values ranging from 0.5 to 0.73. These values are still below one, but they reflect the presence of intermittent or local human impacts, such as limited fishing activities or leaks from nearby urban sources that may contribute to the introduction of small amounts of metals into the marine environment. Station S1 recorded the highest PLI value within the study area, at

0.83. This indicates that it is exposed to a relatively higher metal accumulation than the other sites, although the value does not reach the critical limit, indicating significant pollution. This is due to its location in a port with high marine activity and ship traffic. Overall, the results show that the studied area does not suffer from severe metal pollution, as all values remained below the critical limit. However, the differences in values between stations indicate varying environmental impacts depending on the proximity of each site to various human activities. These data reflect the importance of continuing to monitor the quality of marine sediments, especially at stations that recorded relatively high values, and confirm the need to support environmental management efforts aimed at reducing sources of pollution and improving the quality of the coastal environment, thus contributing to maintaining the environmental balance of the marine area.

Geographical accumulation index (Igeo)

The geoaccumulation index (Igeo) has been calculated for the analyzed metals. It was originally defined by [8]. In order to determine and define metal contamination in sediments, by comparing current concentrations with preindustrial levels. It was also to clarify the extent of heavy metal contamination associated with the sediments, which can be calculated by the following equation:

$$I_{geo} = \log_2 [C_x / (1.5 B_x)]$$

Where:

C_x = the measured concentration of the examined metal "x" in the sediment.

B_x = the geochemical background concentration of the metal "x".

Factor 1.5 = the background correlation factor due to lithogenic effects.

The Geoaccumulation index can be used to the estimation of these pollution processes. Müller has distinguished seven classes of Geoaccumulation index [8] in Table 4. The highest class, class six, reflects 100-fold enrichment above the background values.

Table 4. Müller's classification for the Geo-accumulation index

Igeo value	Class	quality of sediment
0 ≥	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
5 <	6	Extremely polluted

Table 5. Geological Accumulation Index (Igeo) values of heavy metals on the eastern coast of the Tripoli study area

Sit no	Igeo(Fe)	Igeo -Cd	Igeo -Cu	Igeo -Pb	Igeo -Mn	Igeo -Zn
S1	8.07	2.38	-0.48	-3.05	-3.44	-2.59
S2	-7.64	1	-0.26	-2.66	-3.54	-2.16
S3	-7.77	0.87	-1.53	-3.17	-3.74	-2.49
S4	-8.08	-0.27	-2.16	-4.68	-4.15	-3.26
S5	-7.91	-0.03	-1.89	-5.28	-4.34	-3.51
S6	-8.12	0.61	-2.06	-3.38	-4.02	-2.95
S7	-8.36	0.63	-1.18	-3.34	-4.56	-3.13
S8	-8.41	-0.66	-1.68	-3.87	-3.8	-2.42
S9	-8.32	-0.7	-2.02	-4.61	NaN	-2.8
S10	-8.01	-1.1	-0.37	-3.27	-3.7	-3.66
S11	-8.04	0.78	-1.32	-4.12	-4.12	-3.91
S12	-7.84	-2.16	-0.11	-3.24	-3.64	-2.62

Based on the calculated values of the Igeo (geological accumulation index) for heavy metal elements in the sediments of the eastern coast of Tripoli, all samples showed low negative values for iron (Fe) ranging between -7.55 and -8.41, indicating that the sediments are not contaminated with this element and fall within the zero category, which reflects the absence of human influences on iron concentrations due to natural dilution processes such as sedimentation and transport. Cadmium (Cd) recorded positive Igeo values at most stations, ranging from -0.66 to 2.38, with the majority of samples falling into categories one and two, i.e., uncontaminated to moderately contaminated.

Stations S1, S12, and S10 represented the highest levels of accumulation, reflecting the presence of anthropogenic sources associated with marine activities in or near ports. Copper (Cu) showed a marked variation in the Igeo index, ranging between -2.16 and 0.11, with most samples falling into category zero, indicating the absence of clear pollution, except some sites such as S1 and S12, which showed slight accumulation indicators, possibly due to ship activity and marine paints. Lead (Pb) recorded negative values, ranging between -2.66 and -5.28, placing all samples within category zero, i.e., uncontaminated,

and reflecting the absence of any recent sources of pollution with this element. For manganese (Mn), values ranged between -3.44 and -4.56, negative at all sites.

The sediments are classified as zero, indicating that manganese is of natural origin, resulting from weathering or transport without human influence. Zinc (Zn) values ranged between -1.65 and -3.91, all of which fall into zero, meaning they are not contaminated, despite the possibility of weak local sources such as wastewater. In general, the marine sediments on the western coast of Tripoli do not show significant contamination with most of the studied metals, with the exception of cadmium, which is likely to accumulate in some stations, necessitating periodic environmental monitoring, especially in areas with high marine activity.

Conclusion

This study confirms that metal accumulation in sediments varies across locations, with the highest concentrations recorded in the Tripoli Commercial Port, reflecting the direct influence of heavy maritime traffic and industrial and commercial activities. In contrast, samples from the small fishing port showed relatively lower levels, indicating a limited impact from human activities. The study also highlighted the correlation between the concentration of some elements, such as copper (Cu) and iron (Fe), and the total organic matter content, indicating the role of organic matter in stabilizing metals within sediments. Environmental assessment indicators (such as Igeo, EF, and PLI) showed that some elements, particularly copper and cadmium, exceeded natural levels, indicating the presence of cumulative pollution that warrants monitoring. From a practical perspective, these results demonstrate that combining statistical and analytical indicators is an effective tool for monitoring marine pollution levels and distinguishing between natural and anthropogenic sources of metals. The study also emphasizes the importance of monitoring major commercial ports, which are major hotspots of metal pollution. Finally, the results recommend the need for future studies on a larger scale, including different time periods and employing advanced techniques such as geochemical modeling, to better understand the dynamics of mineral accumulation and long-term environmental impacts on coastal systems.

Conflicts of Interest

The author declares no conflicts of interest.

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