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Environmental Pollution Assessment of Some Heavy Metals in the Western Coast of Tripoli, Libya

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ABSTRACT

In this study, heavy metal concentrations were measured in sediments of the western coast of Tripoli, Libya, during the year (2024). Sediments (<63 mm) collected from (10) sites representing the study area were examined and analyzed using atomic absorption spectrometry (AAS). The concentrations of the studied heavy metals in the samples ranged in (micrograms per gram) as follows: iron (202.42-347.21), cadmium (0.219-1.41), copper (9.183-69.64), lead (0.61-6.63), manganese (34.14-108.34), and zinc (7.87-42.11). The enrichment factor (EF) index was used to determine the level of sediment contamination in the study area. The results showed a clear variation in contamination levels. Station 8 recorded the highest enrichment factor values, particularly for cadmium (14.1) and copper (6.96), indicating a strong source of pollution associated with marine and industrial activities. Station 1 recorded much lower levels, with an enrichment factor of 1.14 for copper and 5.57 for cadmium, reflecting a lesser influence from human activities. Results of the geological accumulation index (Igeo) calculations for the samples showed that iron (Fe) was the most contaminated element (highly contaminated), followed by cadmium (Cd) (moderately contaminated in some locations). For copper (Cu) and zinc (Zn), sample S8 recorded moderate contamination, while the remaining samples remained uncontaminated. Lead (Pb) and manganese (Mn) showed no contamination. These results indicate that human activity, particularly industrial and marine, has increased iron and cadmium levels, while the remaining elements remained within normal values. Pollution load index (PLI) values indicate the variability in contamination levels across the studied stations. Most stations (1, 3, 4, 5, 6, and 10) showed values less than 1, indicating no significant metal contamination. Stations 2, 7, and 9 recorded values ranging from 0.59 to 1.04, indicating low to moderate contamination. Station 8 was the most polluted, recording the highest value (1.28) due to heavy marine activity. The results indicate the impact of human activities on marine sediment quality, with areas near ports and industrial facilities experiencing higher contamination levels.

Keywords: (Heavy metals)Sediment contamination , Tripoli, Libya

الملخص العربي

تقييم التلوث البيئي لبعض المعادن الثقيلة في الساحل الغربي لطرابلس، ليبيا

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إجريت هذه الدراسة لقياس تركيزات المعادن الثقيلة في رواسب الساحل الغربي لمدينة طرابلس، ليبيا، خلال عام (2024). تم فحص الرواسب (<63 مم) التي جُمعت من (10) مواقع تُمثل منطقة الدراسة، وتحليلها باستخدام مطيافية الامتصاص الذري (AAS). تراوحت تركيزات المعادن الثقيلة المدروسة في العينات (ميكرو جرام/جرام) على النحو التالي: الحديد (202.42-347.21)، والكادميوم (0.219-1.41)، والنحاس (9.183-69.64)، والرصاص (0.61-6.63)، والمنغنيز (34.14-108.34)، والزنك (7.87-42.11). استُخدم مؤشر معامل الإثراء (EF) لتحديد مستوى تلوث الرواسب في منطقة الدراسة. وأظهرت النتائج تباينًا واضحًا في مستويات التلوث. سجلت المحطة 8 أعلى قيم لمعامل الإثراء، وخاصة للكادميوم (14.1) والنحاس (6.96)، مما يشير إلى مصدر قوي للتلوث المرتبط بالأنشطة البحرية والصناعية. سجلت المحطة 1 مستويات أقل بكثير، مع عامل إثراء قدره

1.14 للنحاس و5.57 للكادميوم، مما يعكس تأثيرًا أقل من الأنشطة البشرية. أظهرت نتائج حسابات مؤشر التراكم الجيولوجي (Igeo) للعينات أن الحديد (Fe) كان العنصر الأكثر تلوثًا (ملوثًا للغاية)، يليه الكادميوم (Cd) (ملوث بشكل معتدل في بعض المواقع). بالنسبة للنحاس (Cu) والزنك (Zn)، سجلت العينة S8 تلوثًا معتدلًا، بينما ظلت العينات المتبقية غير ملوثة. لم يظهر الرصاص (Pb) والمنغنيز (Mn) أي تلوث. تشير هذه النتائج إلى أن النشاط البشري، وخاصة الصناعي والبحري، قد زاد من مستويات الحديد والكادميوم، بينما ظلت العناصر المتبقية ضمن القيم الطبيعية. تشير قيم مؤشر حمل التلوث (PLI) إلى التباين في مستويات التلوث عبر المحطات المدروسة. أظهرت معظم المحطات (1، 3، 4، 5، 6، و10) قيمًا أقل من 1، مما يشير إلى عدم وجود تلوث معدني كبير. سجلت المحطات 2، 7، و9 قيمًا تتراوح بين 0.59 و1.04، مما يشير إلى تلوث منخفض إلى متوسط. كانت المحطة 8 الأكثر تلوثًا، حيث سجلت أعلى قيمة (1.28) بسبب النشاط البحري الكثيف. تشير النتائج إلى تأثير الأنشطة البشرية على جودة الرواسب البحرية، حيث تشهد المناطق القريبة من الموانئ والمنشآت الصناعية مستويات تلوث أعلى.

INTRODUCTION

Water pollution with heavy metals has become a major concern in recent years. Heavy metals are among the most persistent pollutants in ecosystems, such as water, sediments, and biota, due to their resistance to degradation under natural conditions. Heavy metals become toxic when not metabolized by the body and accumulate in tissues under certain environmental conditions, reaching toxic concentrations and causing adverse health effects. Heavy metals in marine sediments have both natural and anthropogenic origins, and their distribution and accumulation are influenced by sediment texture, mineral composition, adsorption and dissolution processes, and physical transport. Metals participate in various biochemical mechanisms, are highly mobile, can affect ecosystems through bioaccumulation processes, and can be toxic to the environment and human life **(Manahan, 2000)**. Sediment pollution is one of the most serious environmental problems in marine ecosystems, as they act as both sinks and sources of pollutants in aquatic systems. Sediment analysis plays an important role in assessing the pollution status of the marine environment **(MÜCHA et al., 2003; PEKEY, 2006)**. Studying the distribution, enrichment, and accumulation of heavy metals in beach sediments is crucial for assessing the potential impact of human activities on the beach environment. The main objectives of the current study were to assess the status of heavy metals in sediment samples from the beach area in the context of the specific impact of small-scale wastewater discharges, using the enrichment factor (EF) and studying the spatial distribution of iron, lead, mercury, and cadmium contents. The geoaccumulation index (Igeo) was calculated to assess heavy metals in sediments. Bottom sediments act as a reservoir for heavy metals and therefore deserve special attention in the planning and design of aquatic pollution research studies. If a large and stable sedimentation basin can be identified and studied, researchers can assess geochemical changes over time and potentially establish baseline levels for comparison and contrast with current conditions. Heavy metals, such as iron, cadmium, lead, copper, manganese, and zinc, are considered serious pollutants of aquatic ecosystems due to their environmental persistence, toxicity, and ability to be incorporated into food chains. Marine sediments can be sensitive indicators for monitoring various pollutants in aquatic environments **(Pekey et al., 2004)**. Heavy metal studies can be important in two main aspects. First, from a public health perspective, attention has been drawn to the need to measure the accumulation of heavy metals, especially those that pose serious health risks to humans (iron, cadmium, lead, copper, manganese, and zinc). Second, from an aquatic environmental perspective, the main problem is preventing biological degradation and identifying sources that threaten ecological balance. In this regard, more abundant metals such as copper, zinc, and manganese may sometimes pose a greater risk than lead, mercury, and cadmiu . The present study aims to investigate the distribution of metals (iron (Fe), cadmium (Cd), lead (Pd), copper (Cu), manganese (Mn), and zinc (Zn) along the western coast of Tripoli, Libya, extending from Tripoli seaport to the fishing port in Al-Sayyad area. To achieve the primary objectives of this study, carbon factor analysis was used to evaluate the distribution of metals on human health and the environment. Samples were collected, purified from sediments, and analyzed according to grain size, total per unit, and mineral group. The sediment results were evaluated based on enrichment factor (EF), New York accumulation index (Igeo), and pollution load index (PLI).

STUDY BOUNDARIES :

The study area is located on the western coast of Tripoli, Libya, on the Mediterranean Sea. It extends from Tripoli Port at 32°54'31.07" N and 13°12'17.33" E to Al-Sayyad Marine Fishing Port at 32°49'32.46" N and 12°57'15.45" E, a distance of approximately 2.5 km.

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

Site no	Latitude (N)	Longitude (E)	Distance among sample (m)	
S1	32°49'51.30"N	12°57'5.76 E	1-2	2500
S2	32°50'21.79"N	12°58'32.75 E	2-3	3100
S3	32°50'54.30"N	13° 0'25.31 E	3-4	3600
S4	32°51'43.05N	13° 2'32.19 E	4-5	3850
S5	32°52'26.21N	13° 4'52.08" E	5-6	3450
S6	32°53'21.28"N	13° 6'49.47" E	6-7	3850
S7	32°54'20.01N	13° 8'59.80" E	7-8	3770
S8	32°55'22.22"N	13°11'4.01" E	8-9	4000
S9	32°56'22.42"N	13° 8'32.12 E	9 :Tripoli seaport	7000
S10	32°52'32.75N	12°58'9.14 E	S10 : Sayyad sea port	6000

It is an open beach that was quickly affected by urban expansion and its sources of pollution include untreated household waste through many small submerged sewage outlets spread along the coast. There are also many small industries such as: car cleaning and repair shops, some food factories, gas stations, small dairy factories, and some factories. Other sewage discharges occur through some outlets.

MATERIALS AND METHODS:

SAMPLING SITES

Approximately one (1) kg of sediment samples were collected during 2024 from 10 sites covering the different study areas (Figure 1 and Table 1). Samples were cut from the center of the catcher using a plastic spoon to avoid contamination with the mineral portion. 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 known to be affected by various activities.

Fig. (1): The positions of sediments samples in the study area.

SAMPLE PREPARATION

The samples were spread in the laboratory on plastic sheets for a few days at room temperature inside a clean cabinet until they dried to a constant weight. They were sieved through a sieve (2 mm) to get rid of pebbles. Then each sample was divided into two sub-samples. One subsample was used for grain size analysis, while the other subsample was homogenized using 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 (18-32gm) 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 **(Folk, R L.1974)** Grain size determination was made on the dried samples by the conventional sieving method. Dry sand was fractioned 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 method described by **(Gaudette and Flight, 1974).**

ANALYSIS OF SEDIMENT SAMPLES

The total concentrations of heavy metals (Iron, cadmium ,Cuprum , lead, Manganese and zinc) the samples were digested in an open system with a mixture of concentrated (HNO_3 / $HClO_4$/ HF) (6:3:1) according to(**Oregioni and Aston, 1984).**

Table (2): Distribution of grain size, total organic carbon, and (heavy metals in micrograms/gram) of sediment samples collected from (the study area)

Site no	Sand (%)	Silt (%)	Clay (%)	TOC %	Heavy metals (µg/g)						Nomenclature
					Fe	Cd	Cu	Pb	Mn	Zn	
S1	99,76	0,24	0	0,033	225	0,557	11,373	2,29	77,76	15,321	Coarse sand
S2	100	0	0	0,022	251	0,6635	27,39	3,52	91,42	22,02	Very Coarse sand
S3	99,7	0,21	0,09	0,054	207,41	0,5728	10,66	2,27	76,07	16,09	Coarse sand
S4	98,23	1,77	0	0,038	217,42	0,327	9,183	1,14	63,22	12.54	Medium sand
S5	99,11	0,89	0	0,04	230,29	0,3916	10,34	0,61	65,43	9,29	Medium sand
S6	86,65	13,35	0	0,051	267,21	0,6853	11,38	3,03	75,55	18,57	Fine sand
S7	98,07	1,63	0,3	0,056	347,21	1,13	32,05	4,8	93,54	24,976	Medium sand
S8	96,08	3,92	0	0,06	345,31	1,41	69,64	6,63	108,34	42,11	Fine sand
S9	97,72	2,18	0,1	0,044	317,11	1,28	50,22	5,618	104,96	27,87	Fine sand
S10	100	0	0	0,02	202,42	0,219	10,38	1,126	34,14	7,87	Coarse sand

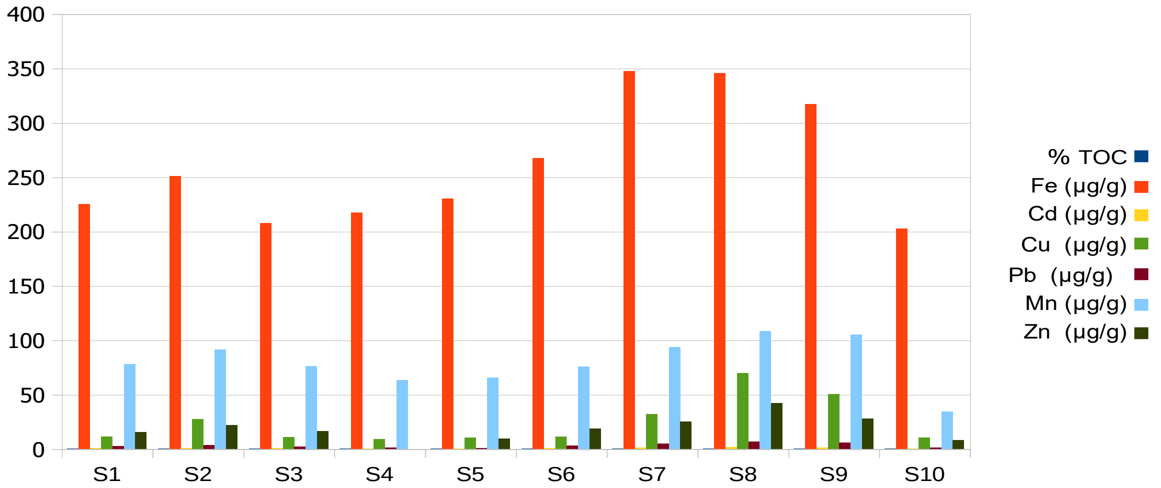

Fig (2) :Concentration of the studied elements and total organic carbon in the study area.

RESULTS AND DISCUSSION

GRAIN SIZE ANALYSIS

It is clear from the data in(Table 2, Fig2) that most of the sediments in the studied area consist mainly of sand with a very high percentage ranging from 86.65% to 100%, the sites that contain 100% very coarse sand (S2 and S10) and more than half of the samples had a high percentage of coarse and medium sand and the sites that contain a lower percentage of sand (S6 and S8). The percentage of silt varied between 0% and 13.35%, where site (S6) represents the only exception with a high silt of 13.35%. With a very slight presence of clay in some sites, not exceeding 0.3% in any site. These results indicate that the region is subject to high energy processes (such as strong sea currents or coastal erosion and marine human activities) that prevent the deposition of fine materials (silt and clay) and make the surface sediments in most sites of a purely sandy nature.

TOTAL ORGANIC CARBON (TOC %)

The results shown in (Table 2, Fig2) the concentration of total organic matter (TOC) was very low in all sites, as the percentage of (TOC) in the studied samples ranged between (0.02% - 0.06%). The lowest concentration of organic matter was recorded in S10 (0.02%), and the highest concentration was recorded in S8 (0.06%). This low percentage was due to the composition of the sediments in this area, which was mainly coarse sand due to the sand not retaining organic matter. Also, the almost complete absence of clay in most sites may be a major reason for the low TOC, since clay has a high capacity to retain organic matter compared to sand. It is noted that there is a correlation between the proportion of fine sediments (Silt + Clay) and organic content, with sites with a higher proportion of silt tending to have relatively higher TOC values. In contrast, sites with 100% sand (S2 and S10) have the lowest TOC levels. **(Zhang et al., 2007)** stated that organic matter increases with decreasing grain size and attributed this to the protective action of silt. Sediments with fine particles provide better surface areas for pollutants to condense than those with coarse particles **(Adesuyi, 2016).** Total organic carbon (TOC) can act as a mediator for heavy metal accumulation as metals adhere to organic matter in sediments.

HEAVY METAL CONCENTRATION :

Heavy metals were analyzed according to the method of **(Oregioni and Aston 1984)**. About 0.2 grams of each sample was placed in a digestion tube and 10 ml of a mixture of three acids, hydrofluoric, nitric and perchloric acids, was added in a ratio of (1:4:6) and left in room temperature for an hour. The digestion tubes were placed on a water valve for 3 hours. After that, the samples were cooled in the laboratory atmosphere and the volume was completed to 25 ml with 1N-HCl acid. 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 m 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 (μgl-1) = (25/W) x μgml-1

By Atomic Absorption Apectroscopy (AAS)

The following table ((2)) shows the values obtained for the percentage of total organic carbon and the analysis of heavy elements (iron, cadmium, copper, lead, manganese, and zinc) using the Atomic Absorption Spectrophotometer (AAS) Shimadzu 6800

IRON

Iron (Fe) is a common mineral in marine sediments, but its concentration may be the result of natural or human sources. The total iron concentration in the sediment samples of the western coast of Tripoli (the study area) was shown in (Table 2, Fig2). The minimum iron concentration (202.42 μg/g) was in sample 10, which was detected in the open area of the sea, where it is far from any source of pollution that may increase the iron concentration in the sediments. Therefore, this sample serves as a reference sample. In addition, this may be attributed to the high sand content (100%) (very coarse sand), as well as the low total organic carbon content (0.02%). On the other hand, the maximum iron concentration (347.21 - 345.31 μg/g) was detected in S 8- S7 respectively, and these samples recorded the highest iron concentration because they are areas with finer sediments (Medium & Fine Sand), and the presence of sample 8 in the port and sample 7 in the path of ships entering and exiting the port, which indicates pollution related to marine and commercial activity. Although both samples (8 1) They are located within the port of Tripoli and Mit Sayyad, respectively, but the recorded iron concentrations were very different, the commercial port (S8) has the highest Fe and TOC% due to high industrial and commercial activity, and pollution from ships. The fishing port (S1) has the least pollution due to low industrial activity and ship traffic, with coarse sediments that reduce the retention of heavy metals. The correlation coefficient between Fe and TOC% = 0.614, indicating a moderate relationship between them, where the more iron, the more organic matter in the sediments. For sites (202.42 - 207- 217.42 - 230.29) (S4, S3, S10 S5) respectively, they contain lower percentages, indicating that they may be less exposed to pollution sources or have more efficient natural cleaning processes. The results showed a low enrichment of iron in the western shores of Tripoli compared to pollution in the northern and eastern Mediterranean regions. The higher content in some samples compared to others is attributed to human activities accompanied by increased amount of household discharge from boats, fishing activities, fueling and maintenance practices. Sediments act as a major sink for pollutants in the aquatic environment as suspended sediment particles deposit the adsorbed pollutants to be removed from the water column. In general, the iron oxidation pathway is affected by many factors (e.g. pH, temperature) **(El-Jaziri et al., 2007).** The results obtained in this study were almost consistent with the study of **(Al-Dhuwaib et al. 2019)** for the Mediterranean sediments in the Libyan coast, which ranged between (230 - 704 µg/g) and to some extent with the study of **(Abdel-Ghani et al., 2021)** in the Zawiya oil port, which ranged between (975: 2771 with an average of 1612 µg/g) for iron. 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 (E**l-Nimr et al., 2007).** It is much lower than that recorded in the sediments of Damietta port, which ranged between (14216-55619 ppm; **(El-Gharbawi, 2013),** and that recorded in the sediments of northwestern Spain (22,970 mg/kg-1;**(Villares et al., 2003).**

CADMIUM

Cadmium (Cd) is a toxic heavy metal found in marine sediments as a result of natural sources or human activities. The concentration of cadmium in marine sediments was determined in the western coast of Tripoli (the study area) as shown in (Table 2, Fig2). The lowest concentration of cadmium (0.219 µg/g) was recorded in sample S10, which was collected from an open area far from potential pollution sources, making it a reference sample. This low concentration can be explained by the high proportion of very coarse sand and the low TOC content (0.02%). The highest concentration of cadmium (1.41 - 1.28 µg/g) was in samples S8 and S9, respectively, as these areas are characterized by sediments (fine and medium sand), which enhance the absorption of heavy metals. Sample S8 is located within the port of Tripoli, a major commercial port with heavy ship traffic, while sample S9 is located in an area close to marine maintenance activities and ship routes. The cadmium concentrations were significantly different between sample S8 (=1.41) and sample S1 (=0.557 µg/g). This difference is attributed to the nature of the activity in each of them, as the port of Tripoli is characterized by high industrial and commercial activity, which leads to high cadmium concentration and increased total organic carbon (TOC = 0.06%). On the contrary, the fishing port is characterized by low industrial activity and ship traffic, with coarse sediments that reduce cadmium accumulation. The correlation coefficient between cadmium and TOC% (r = 0.72) showed a strong positive relationship between them, indicating that increased organic carbon contributes to the accumulation of cadmium in the sediments. For samples with low concentrations such as (S4 = 0.327, S5 = 0.3916, S10 = 0.219, S3 = 0.5728 µg/g), they contain lower levels of cadmium, indicating that they may be less exposed to pollution sources or are subject to effective natural cleaning processes by ocean currents. Compared to previous studies, cadmium levels in this study were higher in some samples affected by ship traffic than those recorded in some industrial areas in the Mediterranean, including Alexandria Port (**Abdul Ghani, et al., 2020)** , ranging from 0.1362 - 0.7136 µg/g) and Zawiya Port **(Jumaa, et al., 2021**). 0.0076 - 0.0718 µg/g) and the cadmium levels were lower than those reported in the study (**Edweb, et al., 2019)** for the Garbouli area (0 - 1.5 µg/g). International environmental standards, including NOAA and EPA, determine the safe thresholds for cadmium concentrations in sediments. (So that (TEL): less than 0.7 µg/g, (PEL): 4.2 µg/g and the levels of the current study were clearly contaminated with cadmium in samples (7, 8, 9), which is the Tripoli port area, indicating the presence of clear contamination in this area only from the studied area. This study confirms that cadmium contamination in marine sediments on the western coast of Tripoli is mainly linked to human activities in ports, which calls for taking appropriate environmental measures to reduce pollution sources and minimize potential environmental risks.

COPPER

Copper (Cu) is a heavy metal found in marine sediments as a result of natural sources or human activities. The concentration of copper in marine sediments was determined in the western coast of Tripoli (study area) as shown in(Table 2, Fig2).The lowest concentration of copper (9.183 µg/g) was recorded in sample S4.This low concentration can be explained by the high proportion of medium sand and low TOC content (0.038%). The highest concentration of copper (69.64-50.22 µg/g) was in sample S8 and S9 respectively, as these areas are characterized by sediments (fine sand), which enhances the absorption of heavy metals. Sample S8 is located within the port of Tripoli, a major commercial port with heavy ship traffic, while sample S9 is located in an area close to marine maintenance activities and ship routes. Copper concentrations differed significantly between sample S8 (=69.64) and sample S1 (=11.373 µg/g), and this difference is attributed to the nature of the activity in each of them, as Tripoli port is characterized by high industrial and commercial activity, which leads to high copper concentration and increased total organic carbon (TOC = 0.06%). In contrast, the fishing port is characterized by low industrial activity and ship traffic, with coarse sediments that reduce copper accumulation. The correlation coefficient between copper and TOC% (r = 0.72) showed a strong positive relationship between them, indicating that increased organic carbon contributes to copper accumulation in the sediments. As for the samples with low concentrations such as (S4 = 9.183, S5 = 10.34, S10 = 10.38, S3 = 10.66 µg/g), they contain lower levels of copper, indicating that they may be less exposed to pollution sources or subject to effective natural cleaning processes by ocean currents. Compared to previous studies, copper levels in this study ranged from (9.183 - 69.64 µg/g) and were higher than the results (**Abdul-ghani et al., 2020),** ranging from 8.2 - 45.6 µg/g), and lower than the results in Zawiya port **(Juma et al., 2021)** ranging from 136.1 - 1006.2 µg/g). Copper levels were lower and relatively close to the results mentioned in the study (**Edweb, et al., 2019**) for the Qarbouli area (15 - 72 µg/g). International environmental standards, including NOAA and EPA, specify safe thresholds for copper concentrations in sediments. (TEL: less than 30 µg/g, PEL: 150 µg/g). The levels of the current study were clearly contaminated with copper in samples (7, 8, 9), which is the Tripoli port area, indicating the presence of clear pollution in this area only from the studied area. This study confirms that copper pollution in marine sediments on the western coast of Tripoli is mainly linked to human activities in ports, which calls for taking appropriate environmental measures to reduce pollution sources and minimize potential environmental risks

LEAD

Lead (Pb) is a heavy metal found in marine sediments as a result of natural sources or human activities. The concentration of lead in marine sediments in the western coast of Tripoli (study area) was determined as shown in (Table 2 , Fig 2) . The lowest concentration of lead (0.61 µg/g) was recorded in sample S5. This low concentration can be explained by the high proportion of medium sand and the low total organic carbon content (0.04%). The highest concentration of lead (6.63 - 5.618 µg/g) was in sample S8 and S9 respectively, as these areas are characterized by fine sand sediments that enhance the absorption of heavy metals. Sample S8 is located within the port of Tripoli, a major commercial port with heavy ship traffic, while sample S9 is located in an area close to marine maintenance activities and ship routes. The concentrations of lead differed significantly between sample S8 (=6.63) and sample S1 (=2.29 µg/g). This difference is attributed to the nature of the activity in each of them, as the port of Tripoli is characterized by high industrial and commercial activity, which leads to high concentrations of lead and an increase in total organic carbon (TOC = 0.06%). The correlation coefficient between lead and TOC% (r = 0.72) showed a strong positive relationship between them, indicating that the increase in organic carbon contributes to the accumulation of lead in the sediments. As for the samples with low concentrations such as (S4 = 1.14, S5 = 0.61, S10 = 1.126, S3 = 2.27 µg/g) they contain lower levels of lead, indicating that they may be less exposed to pollution sources or subject to effective natural cleaning processes by ocean currents. Compared to previous studies, lead levels in this study ranged from (0.61 - 6.63 µg/g) and were higher than the results (**Abdul ghani et al. 2020)** which range from 0.5 - 3.5 µg/g) and lower than the results in Zawiya port (**Jumaa et al. 2021) ,** which range from 12.0 - 100.0 µg/g). Lead levels were lower and relatively close to the results mentioned in the study (**Edweeb et al. 2019)** for the Qarbouli area 2.0 - 5.0 µg/g). International environmental standards including NOAA and EPA set safe thresholds for lead concentrations in sediments (TEL: less than 30 µg/g, PEL: 150 µg/g). The levels in the current study showed clear lead contamination in Tripoli port and the areas Very close to it is the most polluted area with lead compared to the results of the current study, as the pollution appears significantly in sample S8 (6.63 µg/g) and sample S9 (5.618 µg/g). This pollution is mainly related to human activities in the port.

MAGNESIUM

Magnesium (Mn) concentration was determined in marine sediments of the western coast of Tripoli (study area) as shown in (Table 2, Fig2). The lowest Mn concentration (34.14 µg/g) was recorded in sample S10. The highest Mn concentrations (108.34 - 104.96 µg/g) were recorded in samples S8 and S9, respectively. Mn concentrations differed significantly between sample S8 (= 108.34) and sample S1 (= 77.76 µg/g). This difference is attributed to the nature of the activity and movement of ships and boats, which led to a higher Mn concentration and an increase in total organic carbon (TOC = 0.06%) in S8. In contrast, site S1 has low industrial activity and ship movement, with coarse sediments that reduce Mg accumulation, and this comparison borders the studied area. The correlation coefficient between magnesium and TOC% (r = 0.72) showed a strong positive relationship, indicating that increased organic carbon contributes to magnesium accumulation in the sediments. Samples with lower concentrations, such as S10 = 34.14, S5 = 65.43, and S3 = 76.07 µg/g, contained lower levels of magnesium, indicating that they may be less exposed to fewer pollution sources. Magnesium levels in this study ranged from 34.14 to 108.34 µg/g, higher than the results reported by (**Abdelghani et al., 2020)**, which ranged from 20 to 80 µg/g, and lower than the results reported by Zawiya Port (**Juma et al., 2021**), which ranged from 120 to 400 µg/g. Magnesium levels were also closer to the results reported by (**Edweb et al., 2019**), for the Garabouli area (30 to 100 µg/g). According to NOAA and EPA, the current study showed magnesium contamination levels in samples (8 and 9) in the Tripoli port area. This study confirms that this contamination is mainly related to human activities in the port.

ZINC

Zinc (Zn) concentrations in the marine sediments of the study area were determined as shown in Table 2, Figure 2. The lowest Zn concentration (7.87 mg/kg) was recorded in sample S10, while the highest Zn concentrations were recorded in sample S8 (= 42.11 mg/kg), followed by sample S9 (= 27.87 mg/kg). Zn concentrations varied significantly between sample S8 and sample S1 (= 15.321 mg/kg), which is attributed to the nature of the intensive maritime activity in the port of Tripoli, where ship traffic and industrial discharges led to high Zn concentrations and increased total organic carbon (TOC = 0.06%) in sample S8. In contrast, some areas, such as S1, were characterized by low industrial activity and less ship traffic, with coarse sediments that reduced Zn accumulation, resulting in lower levels of contamination. The correlation coefficient between zinc and total organic carbon (r = 0.75) showed a strong positive relationship, indicating that increased organic matter contributes to zinc accumulation in marine sediments. Zinc levels in this study ranged from 7.87 to 42.11 mg/kg, which is lower than the results of (**Edweb et al.2019**) (33 - 105 mg/kg). According to the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA), zinc levels in some samples, particularly S8 and S9, indicate the presence of pollution resulting from anthropogenic activities in the area. According to NOAA and EPA, the current study showed that zinc pollution levels in samples 8 and 9 in the Tripoli Harbor area are mainly associated with anthropogenic 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 **(Daskalakis and O'Connor, 1995; Feng et al., 1998)**. 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 **(Feng et al., 1998; Mucha et al., 2003).** According to (**Ergin et al., 1991)**, the metal enrichment factor (EF) is calculated using the following equation:

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

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).

In Table 3 and Figure 3 show the pollution levels at ten stations in the study area, based on the enrichment factors (EF) for a group of heavy metals, namely cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), and zinc (Zn), as well as the general pollution index (PLI). The results indicate a clear variation in pollution levels between stations, with Station 8, located in the large commercial port of Tripoli, showing the highest pollution levels compared to the rest. This station recorded the highest values for enrichment factors, particularly for cadmium (14.1) and copper (6.96), indicating a strong source of pollution, often associated with intensive industrial and marine activities, such as oil spills, the use of corrosion-resistant paints, and the disposal of marine waste. The general pollution index (PLI) at this station was 1.28, the highest among all stations, confirming that the area suffers from severe pollution. On the other hand, Station 1, located in a small fishing port, recorded much lower pollution levels, with a copper enrichment factor of only 1.14, while the cadmium enrichment factor did not exceed 5.57. The General Pollution Index (PLI) at this station did not exceed 0.33, reflecting an environment less affected by industrial activities, given the port's fishing-based nature and its lack of large ship traffic or significant industrial activity. Overall, the data reveal a clear impact of human activities on pollution levels, with heavy metal concentrations significantly increasing in areas with high marine density, such as Tripoli Port. It is worth noting that manganese appears at elevated values at most stations, potentially indicating a natural source, in addition to other environmental influences. Based on these results, it is recommended to strengthen environmental monitoring programs, especially in commercial ports, to reduce the accumulation of heavy metals in marine sediments. It is also recommended to implement marine litter management strategies, such as improving port waste treatment systems and reducing the discharge of oils and pollutants into the water. Finally, additional studies, including analysis of water samples and suspended matter, are needed to more precisely understand the sources of pollution and develop effective solutions to reduce it.

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

Stations	Cd EF	Cu EF	Pb EF	Mn EF	Zn EF	PLI
1	5,57	1,14	0,11	18,98	0,31	0,33
2	6,64	2,74	0,18	19,71	0,44	0,59
3	5,73	1,07	0,11	18,26	0,35	0,35
4	3,27	0,92	0,06	14,77	0,25	0,19
5	3,92	0,93	0,03	15,16	0,19	0,19
6	6,85	1,14	0,15	16,74	0,37	0,36
7	11,3	3,21	0,24	20,35	0,5	0,6
8	14,1	6,96	0,33	22,33	0,84	1,28
9	12,8	5,02	0,28	22,05	0,56	1,04
10	2,19	1,04	0,06	10,9	0,16	0,29

POLLUTION LOAD INDEX

To investigate the pollution state in the study area, pollution load index (PLI) was computed according to Tomolison et al.,(1980) using the following equation:

PLI = (CF1 x CF2 x ………CF n)1/n

Where:

PLI = Pollution load index.

CF = Contamination factor which is equal to the concentration of the metal in 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 (Saleh, 2006).

The calculated Pollution Load Index (PLI) values for the study stations indicate a clear variation in pollution levels across the studied area. Most stations, such as stations 1, 3, 4, 5, 6, and 10, showed values less than 1, indicating that these sites were not exposed to significant metal pollution, or that natural processes such as sedimentation and dilution contributed to limiting metal accumulation. Stations 2, 7, and 9 recorded values ranging from 0.59 to 1.04, indicating low to moderate pollution levels, potentially resulting from limited local pollution sources or intermittent human influences. Station 8, on the other hand, was the most polluted of all stations, recording the highest PLI value of 1.28. This is consistent with its geographical location in the commercial port of Tripoli, where heavy maritime activity, large ship traffic, and industrial discharges increase the potential for metal contaminants to accumulate in surface sediments. In general, these values reflect the impact of various human activities on marine sediment quality. Areas close to ports and industrial facilities are associated with higher pollution levels, while areas farther from major pollution sources maintain better environmental quality. These results can help guide environmental management strategies and implement measures to reduce marine pollution in the most affected areas.

GEOACCUMULATION INDEX (Igeo)

Geoaccumulation index (Igeo) has been calculated for analyzed metals. It was originally defined by **Müller (1979).** In order to determine and define metals contamination in sediments, by comparing current concentrations with preindustrial levels. It was also to clarify the extent of heavy metals contamination associated with the sediments and can be calculated by the following equation:

$$\mathbf{Igeo = \log_2 [Cx / (1.5\ Bx)]}$$

Where:

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

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

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

The Geoaccumulation index can assess to the estimation of these pollution process. Müller has distinguished seven classes of Geoaccumulation index (**Müller, 1981**) in table (4).The highest class class six reflects 100-fold enrichment above the background values.

Table. (4): Müller's classification for Geo-accumulation index (Müller, 1981).

Igeo value	class	Quality of sediment
≤ 0	0	Unpolluted
0-1	1	From un polluted 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 extremelpolluted
> 5	6	Extremely polluted

Table 5: Geological Accumulation Index (Igeo) values for heavy metals on the western coast of Tripoli (study area)

Stations	Igeo(Fe)	Igeo -Cd	Igeo -Cu	Igeo -Pb	Igeo -Mn	Igeo -Zn
S1	5,81	0,31	-2,14	-4,54	-3,79	-2,63
S2	5,97	0,55	-0,74	-3,93	-3,41	-2,05
S3	5,69	0,34	-2,22	-4,55	-3,82	-2,55
S4	5,76	-0,3	-2,56	-5,81	-4,18	-3,09
S5	5,85	-0,06	-2,29	-6,71	-4,12	-3,82
S6	6,06	0,61	-2,14	-4,17	-3,85	-2,39
S7	6,44	1,32	-0,49	-3,39	-3,2	-1,87
S8	6,43	1,66	0,62	-2,87	-2,92	-0,9
S9	6,31	1,5	0,15	-3,14	-2,97	-1,65
S10	5,66	-0,61	-2,3	-5,83	-5,38	-4,31

Based on the calculated values of the geological accumulation index (Igeo) shown in Table (5) for sediment samples from the western coast of Tripoli (the study area), the level of heavy metal contamination in marine sediments was analyzed and interpreted as follows: Iron (Fe): All samples showed high Igeo values ranging from 5.66 to 6.44, indicating that the sediments are classified as category (5-6) (highly to very highly polluted). Cadmium (Cd): Igeo values ranged from -0.61 to 1.66, with most samples falling into category (1-2) (from unpolluted to moderately polluted). Samples (S7, S8, and S9) represent the highest levels of cadmium contamination, indicating anthropogenic sources of contamination. Copper (Cu): Copper Igeo values show a clear variation, ranging between -2.56 and 0.62. Most samples fall into category (0) (uncontaminated), with the exception of sample (S8), which falls into category (1) (uncontaminated to moderately contaminated). These values can be attributed to marine activity and the influence of marine fuels and paints. Lead (Pb): All Igeo values were negative, ranging between -6.71 and -2.87, indicating that all samples fall into category (0) (uncontaminated). This reflects the absence of lead pollution effects in this area. Manganese (Mn): Igeo values range between -5.38 and -2.92, with all samples falling into category (0) (uncontaminated). Zinc (Zn): Zinc Igeo values show a variation between -4.31 and -0.90. Most samples fall into category (0) (uncontaminated), with the exception of sample (S8), which falls into category (1) (from uncontaminated to moderately contaminated). Therefore, the calculated values of the geological accumulation index indicate that iron is the most contaminated element in the sediments of the western coast of Tripoli, followed by cadmium in some locations. The other elements remain within the natural limits without obvious contamination. This is due to human influences such as industrial and maritime activity, in addition to natural geological factors that affect the distribution of metals in the sediments.

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