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Assessment of the presence of heavy metals in the Libyan Sea coast

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Abstract

Heavy metals are highly enduring pollutants in ecosystems, including water, sediments, and biota, due to their resistance to decomposition in natural settings. To detect the presence of heavy metal pollutants residential (group A), civilian (group B), and industrial (group C) zone of Libyan coastline, a total 24 samples (12 surface water samples, 6 soil samples, and 6 sand samples) were collected for the determination of Cr, Cd, Cu, Pb, Ni, Mn, Zn and Fe using atomic absorption spectrophotometer at specific wavelengths. Results showed that samples collected from coastline near industrial zone consists of highest concentration of Cr i.e. 1.318, 1.360, 1.404, 1.437, 1.572, 1.615, 1.550 and 1.595 from water, sand and soil samples (C_1W, C_2W, C_3W, C_4W, C_5 30, C_5 70, C_6 20, C_6 50) respectively while Pb, Ni, Fe were low. While minimum concentration of Cr was observed in samples collected from residential area. Lowest value of Cd (0.014) was found in sand sample collected from beach near industrial zone at 30cm depth. Its highest value (0.3428) was also observed in water sample from beach of industrial zone. Cu concentration is maximum (0.1496) in sand sample collected from 30cm depth at beach of residential area. Nickel and copper was <0.1 in all samples. Lead was highest in sand sample at 30cm depth from beach of residential area while in civilian and industrial zone it was <0.1. Maximum Mn was observed in sand sample of 70cm depth from civilian zone. Zinc concentration was maximum in soil sample collected from beach near industrial zone at 50cm depth. The assessment of surface water quality reveals significant contamination in all zones, with chromium (Cr) and cadmium (Cd) exceeding EPA standard values for seawater. The study emphasizes the influence of anthropogenic activities, especially industrial and agricultural practices, on surface water pollution.

Keywords: *Heavy metals, Libyan Sea coast, atomic absorption spectrophotometer, Soil & water samples.*

1. Introduction

Heavy metals are highly enduring pollutants in ecosystems, including water, sediments, and biota, due to their resistance to decomposition in natural settings. Their toxicity becomes evident when they surpass essential levels. Heavy metals pose a significant threat to human health and the environment with a density exceeding 5 g cm-3 (Tchounwou, et al., 2012). In recent years, the contamination of soil and aquatic environments by heavy metals has become a grave global concern, primarily resulting from human activities driven by increased industrialization and urbanization (Dabaradaran et al., 2010; Qiu, et al., 2019).

There is a widespread acknowledgment today that the behaviour of heavy metals in the environment is primarily influenced by their specific physicochemical fractionation, speciation, or chemical form, rather than solely by their overall concentration (Tack and Verloo, 1995). In sediment environments, trace metals have the potential to distribute themselves among various forms, including exchangeable, acid-soluble (associated with carbonates), reducible (linked to Fe/Mn oxides and hydroxides), oxidizable (related to organic matter), and residual (tied to silicates and detrital materials) species.

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Iron (Fe), copper (Cu), zinc, and manganese (Mn) are important metals since they play significant roles in biological systems (Hogstand and Haux, 2011) but they become toxic at higher concentrations. Metals that are not essential to biological systems, such as lead (Pb) and cadmium (Cd), possess potent toxicity even at relatively low concentrations. The accumulation of these metals in tissues can result in intoxication, cellular and tissue damage, reduced fertility, impaired organ function, and cell death (Damek-Proprawa and Sawicka-Kapusta, 2003). The real causes of this inclusion of dangerous metals include various industries like tanneries, textiles, paint, and lead-water batteries (Nayl, et al., 2017).

Predominantly, heavy metals like Cd, Pb, and Hg exhibit high toxicity toward the biochemical reactions that take place within living organisms. Consequently, these metals tend to accumulate within the edible organs of aquatic animals, such as the spleen, viscera, kidneys, and liver, among others (Yaqoob, et al., 2020). Consuming contaminated seafood can lead to detrimental consequences on human health, particularly due to the presence of toxic heavy metals. These metals can inflict harm on multiple organs, potentially causing various illnesses or even resulting in fatalities (Jaishankar, et al., 2014).

Certain heavy metals like cadmium, chromium, lead, and arsenic share similarities with essential metals such as iron, zinc, manganese, and copper. However, these heavy metals are harmful when present in small quantities throughout the food chain, posing an exceptional threat to animals, plants, and humans.

Within an aquatic ecosystem, organisms rely on sediments as a food source. However, when these sediments become contaminated with toxic heavy metals, they absorb and accumulate these metals at levels significantly higher than those found in the surrounding aquatic environment. As a result, these sediment-based reservoirs of toxic heavy metals become a secondary contributor to marine water pollution. (Pandiyan et al., 2021)

When these dangerous compounds come into contact with benthic organisms, they disrupt the entire coastal food chain. When sediments are contaminated, they may serve as a water supply for heavy metals. (Zhong et al., 2006). Numerous studies have followed the presence of heavy metals in sediments from coastal areas (Omar et al., 2015; Alharbi and El-Sorogy, 2017). Extensive research has provided evidence of elevated concentrations of heavy metals in sediments across various regions worldwide. Moreover, heavy metal pollution poses a significant and enduring environmental challenge on a global scale, especially in coastal areas due to substantial inputs from both natural processes and human activities (Cao, et al., 2017).

Libya Situated in North Africa, is a nation known for its expansive flat terrain. With a steadily growing population and increasing industrial capacity, there is mounting pressure on natural water resources to meet present and future needs for both domestic and industrial purposes. Libya's economy heavily relies on the oil industry, as it is a major producer of oil and gas. Throughout the country, onshore and offshore, oil and gas facilities are scattered, resulting in a substantial demand for water in terms of both quality and quantity (Al-Hengari, et al., 2007).

Water availability and the depletion of underground water due to excessive usage in agricultural projects are among the primary environmental issues in Libya. These practices have led to increased salinity and the intrusion of seawater into coastal aquifers. Additionally, the coastal environment faces a substantial environmental challenge in the form of water pollution resulting from a combination of sewage, oil by-products, and industrial waste (El Haddad, 2012). Though Libya has the largest African Mediterranean coast, almost 1770 km (Barich et al., 2006), limited studies have been done on the distribution of heavy metals in coastal sediments (El Haddad, 2012).

The Libyan coastline boasts the longest stretch along the Mediterranean Sea among African countries. Apart from its impressive length, it is also abundant in natural resources, including abundant fish stocks and valuable energy and mineral resources. Conducting a comprehensive study on the distribution, enrichment, and accumulation of metals along the Libyan coast is crucial to evaluating the potential impact of human activities on seawater. However, the existing information currently accessible lacks the necessary precision and comprehensive details (Hasan and Islam, 2010).

The ecosystem health of the aquatic sediments has therefore always been one of the prerequisites to comprehending pollution in the aquatic environment (Bashir, et al., 2020). The assessment of heavy metals in coastal areas and beaches holds significance as these metals can serve as ecological indicators of pollution. The primary objective of this study is to examine the geographical distribution of heavy metal concentrations in different regions along the Libyan Sea coast.

By analysing the heavy metal levels, it aims to identify highly contaminated areas within the coastal zones, including rural, civilian, and industrial areas. The investigation of heavy metal concentrations will facilitate the identification of various pollution indicators. Additionally, using multivariate statistical methods, the study aims to determine both natural and human sources of specific metals within the research area. Furthermore, the environmental consequences of heavy metal contamination in the study area will be evaluated with reference to standards set by the Environmental Protection Agency (EPA) or World Health Organization (WHO).

2. Material and methods

Study area

The study was done at three localities of Libyan coastline i.e. rural zone, civilian zone, and industrial zone. A total of 24 surface water and soil samples were collected and preserved in polythene bags. Eight samples were collected from different locations (table 1) of each zone including 4 water samples two soil and two sand sample. The sediment samples were carefully weighed 1 gram of each sample and placed into a clean and dry Teflon vessel designed for microwave

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digestion. The samples were then subjected to digestion by combining 3 ml of HCl, 1 ml of HF, and 1 ml of HNO3. After filtration the de-ionized water was used to dilute the samples and for preparation of working standards. The samples were analyzed for different heavy metals (Cr, Cd, Cu, Pb, Ni, Mn, Zn, and Fe) at specific wavelength through atomic absorption spectrophotometer by using the protocol of AOAC (A.O.A.C., 1990).

Table 1: Locations of areas from where samples were collected

Sample	Locations	
	Latitude	Longitude
A1 (Water)	32.908030	13.231363
A2 (Water)	32.910435	13.230622
A3 (Water)	32.912486	13.229711
A4 (Water)	32.914178	13.228922
A5 (Sand)	32.908030	13.231363
A6 (Soil)	32.903741	13.232515
B1 (Water)	32.710259	14.177595
B2 (Water)	32.711961	14.179163
B3 (Water)	32.713796	14.180895
B4 (Water)	32.715002	14.182745
B5 (Sand)	32.710182	14.177561
B6 (Soil)	32.707029	14.174187
C1 (Water)	32.628584	14.328155
C2 (Water)	32.630874	14.328898
C3 (Water)	32.633138	14.329990
C4 (Water)	32.635263	14.330900
C5 (Sand)	32.628470	14.328014
C6 (Soil)	32.624936	14.324857

Samples analysis

The samples underwent di-acid digestion, involving the combination concentrated perchloric acid ($HClO_4$) and nitric acid (HNO_3). 0.5g air-dried soil sample (0.15 mm) was taken into calibrated digestion tube. In the same tube concentrated HNO_3 was added and placed the tube into rack and the rack into block digestor. A glass funnel was placed in the neck of the tubes. Initially, the temperature was set at 145 °C for 1 hour. After 1 hour concentrated $HLCO_4$ was added and increased the temperature to 240° C for further 1 hour. The tube rack was lifted out from the block digestor and placed carefully on rack holder. The tubes were left to cool at room temperature. Following digestion, filtration was carried out using Whatman filter paper no. 42, and de-ionized water was utilized for sample dilution and the preparation of working standards. The filtrate obtained from the samples was adjusted to a volume of 50 ml with distilled water. Chemical analyses were conducted on both soil and sediment samples using flame atomic absorption spectrometry with Varian Spectra AA 220 atomic absorption spectrometer.

Results and Discussion

In the present study the surface soil and water samples from Libyan Sea coast were collected for the determination of heavy metals. Concentration of heavy metals that were chromium (Cr), Cadmium (Cd), Cupper (Cu), Lead (Pb), Nickle (Ni), Manganese (Mn), Zinc (Zn), and Iron (Fe), were measured in the samples of sand, soil, and water collected from beach of residential, civilian and industrial areas. Sand samples were taken at the depth of 30 and 70 cm, whereas the soil samples were collected from 500 m distance from beach at the depth of 20 and 50 cm. While the four water samples were collected from different distances from the beach. The first one was taken from water on the beach, the second from a distance of 250 m from the beach, third from the 500 m distance, and the forth sample was collected from 700 m distance from the beach.

Data presented in figure 1 showed that the Cr concentration in sand sample of industrial area of 30 cm depth was significantly over than the civilian and residential areas. While the presence of Pb, Ni, and Fe was less than 0.1 mg kg^{-1} in the industrial zone. Cadmium was the second most present metal in the depth of 30 cm of the civilian area, however; Cr was less in the residential and civilian areas. Data in figure 2 showed that the concentration of chromium (Cr) was highest in the sand sample collected from 70 cm depth of the industrial area that was slightly over than 1.6 mg kg^{-1} followed by the 1.362 mg kg^{-1} found in the sample taken from civilian area at the same depth. Numerical data exhibited that the nickle (Ni), lead (Pb), and iron (Fe) concentrations were negligible. After Cr, the presence of manganese (Mn) was found considerable that was noted just over than 0.8 mg kg^{-1} in civilian area and just below of 0.8 mg kg^{-1} in industrial zone. The concentration of cupper (Cu) was 0.115 mg kg^{-1} in sand sample collected from residential area and that was significant as compared to Cu concentration found in the samples of sand taken from same depths of civilian and industrial areas.

Concentration of heavy metals in soil sample of 20 and 50 cm depth, and from 500 m away from the beach showed in figure 3. The recorded data showed that Cr metal concentration was maximum as compared to all other metals in all samples while the presence of Fe, Zn, Ni, and Pb was the lowest. The highest concentration of Cr was recorded in the sample of industrial soil of 50 cm depth, that was 1.6 mg kg^{-1} whereas in soil of 20 cm depth of industrial area was near about 1.6 mg kg^{-1}. In soil sample collected from the civilian area the Cr was almost in same concentration (approximately 1.4 mg kg^{-1}) at both depths i.e 20 and 50 cm. After Cr the manganese (Mn) was the most found metal in industrial and civilian areas. The Mn concentration was almost 0.8 mg kg^{-1} in depths of 20 and 50 cm in both civilian and industrial areas.

Analysis of water samples collected from different areas and different distances (Figure 4, 5, 7&8) showed that just Cr concentration was significant in all recorded samples. The maximum Cr concentration was found in water sample collected from industrial area followed by civilian and then residential area. Amongst the selected areas the highest concentration was found in samples taken from industrial area from 700 m distance from the beach and it was 1.437 mg kg^{-1} followed by 1.404, 1.360, and 1.318 mg kg^{-1} in the water samples taken from 500 m, 250 m and on beach water. Civilian area also showed notable concentration of Cr that

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was 1.181, 1.062, 1.008, and 0.9239 mg kg^{-1} in the samples collected from 700 m, 500 m, 250 m, and from on beach. Presence of Cu, Cd, and Zn was notable after Cr in the water sample of on beach. While, in the sample of 700 m, 500 m, and 250 m distances just Cd and Cu was recorded considerable. Concentration of Pb, Ni, and Fe was not found in any water sample of selected areas at any distance. While Mn was detected in samples taken from industrial zone at all distances. It was notable that, Mn contents were found approximately 0.4 mg kg^{-1} in all industrial area at all distances water samples. Cadmium concentration was highest in water sample of beach water that was slightly over than 0.3 mg kg^{-1} while Cd contents were less than 0.1 mg kg^{-1} in water samples taken from 250 and 500 m distances. However, non-significant concentration of Cd was present in the water sample of 700 m distance. Cadmium concentration was less than 0.1 mg kg^{-1} in water samples of 250, 500, and 700 m distances of residential area. Cupper contents were almost same in all selected areas and distances that were less than 0.1 mg kg^{-1}. Presence of Zn was 0.2156 mg kg^{-1} in water sample of industrial area at 700 m distance from beach which was highest concentration of Zn in all measured samples, after that sample the Zn was observed in samples taken from on beach water of civilian and residential areas and it was 0.1323 and 0.1340 mg kg^{-1}.

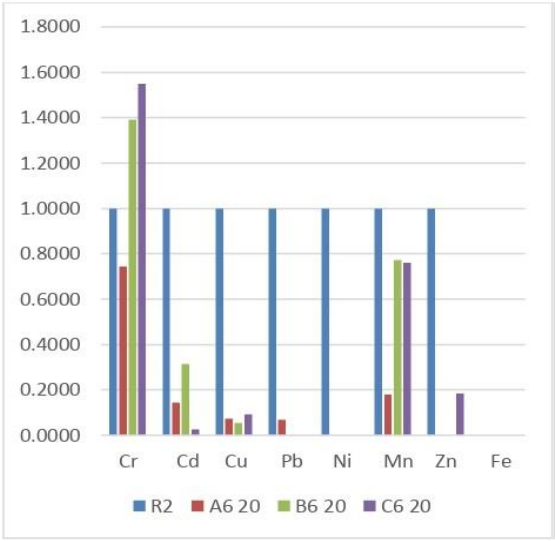

Fig. 1

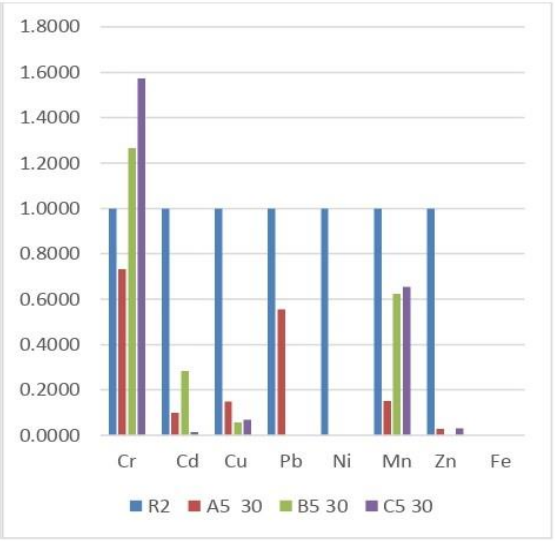

Fig. 2

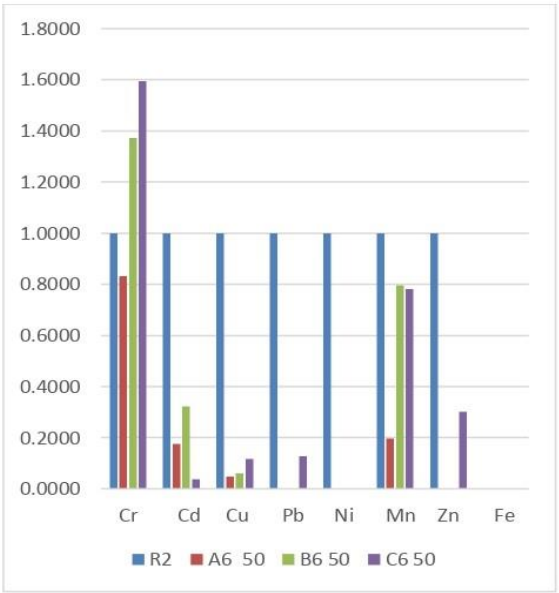

Fig. 3

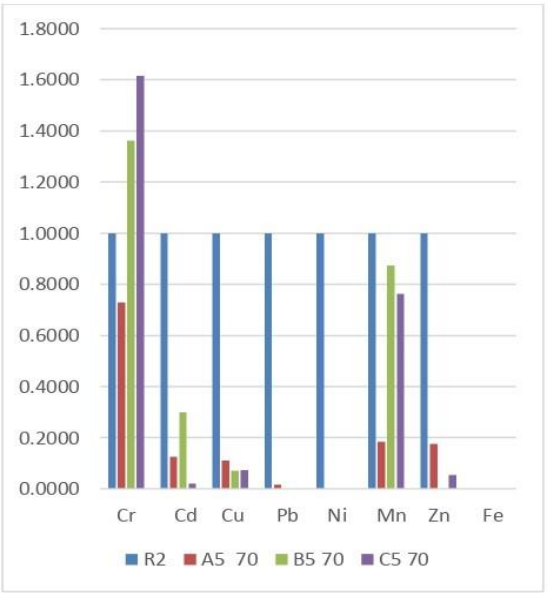

Fig. 4

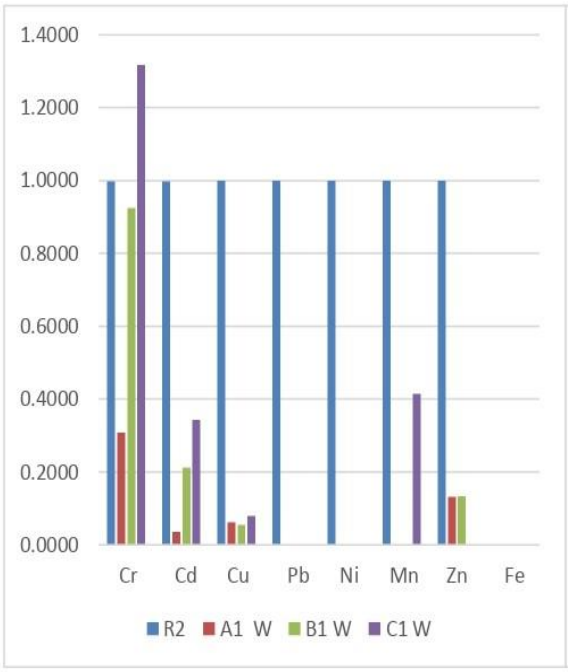

Fig. 5

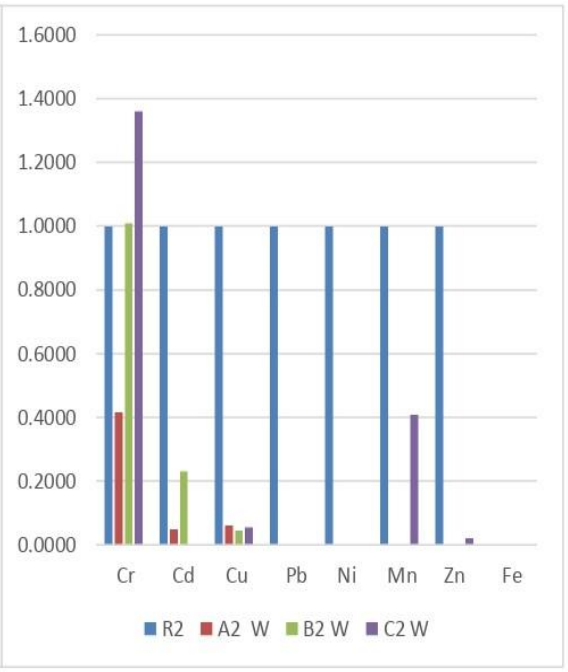

Fig. 6

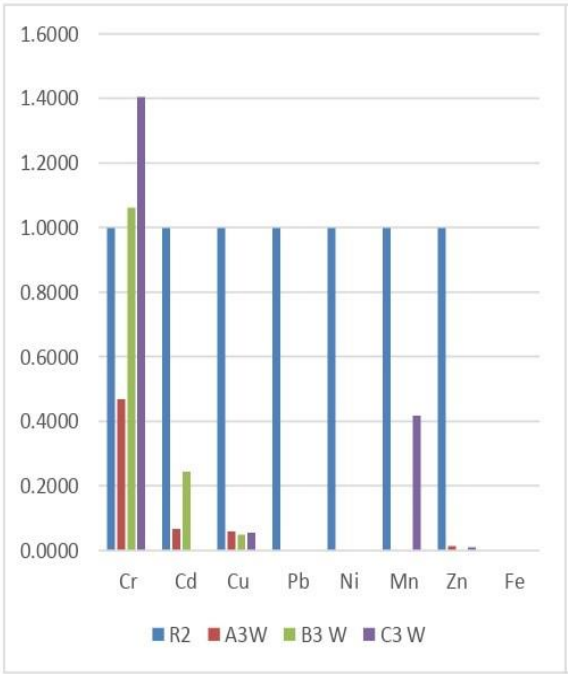

Fig. 7

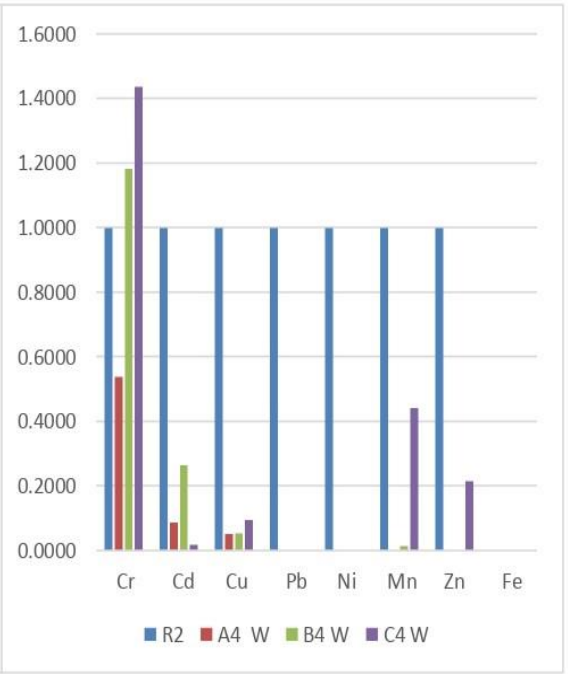

Fig. 8

The results show a positive correlation between the location of samples collection and the concentration of metals. Whereas the average concentrations of heavy metal in group B and C are more than samples of group A.

Sample name	Group A (Residential area)	Group B (Civilian area)	Group C (Industrial area)	location
Water	A_1W	B_1W	C_1W	From sea water on beach
Water	A_2W	B_2W	C_2W	Sea water at 250m distance from beach
Water	A_3W	B_3W	C_3W	Sea water at 500m distance from beach

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Water	A_4W	B_4W	C_4W	Sea water at 700m distance from beach
Sand	A_5 30 A_5 70	B_5 30 B_5 70	C_5 50 C_5 70	Sand sample from beach at 30 and 70cm depth
Soil	A_5 20 A_6 50	B_5 20 B_6 50	B_5 20 B_6 50	Soil sample at 500m distance from beach and from 20 and 50 cm depth

The average concentration of heavy metal such as chromium (Cr), Cadmium (Cd), Cupper (Cu), Lead (Pb), Nickle (Ni), Manganese (Mn), Zinc (Zn), and Iron (Fe) vary according to location and sample type. The concentration of Cr in industrial and civilian area is more than standard Cr concentration. The highest concentration of Cr that is 1.61 from industrial was observed in C_5 70 sample. While its lowest concentration (0.308) was observed in beach water sample (A1 W). From civilian area maximum Cr concentration was observed from B_6 20 sample.

The highest concentration of Cd is present in water sample collected of A_6 20 and A_6 50 samples. However maximum Cd concentration i.e. 0.323 and 0.342 was observed in B_6 50 and C_1W respectively but lowest concentration was observed in C_5 30 and C_4W which is 0.014 and 0.018 respectively. Maximum level of Cu was observed in A_5 30 (0.149) and B_2W (0.44). The concentration of Pb, Ni, and Fe from all samples was observed less than 0.1 except A_4W where its concentration is 0.5547 (Mao et al., 2019). In B_5 70 the maximum value of Mn is present (0.8726) and lowest value is present in B_4W (0.014). The highest levels of chromium (Cr) and Cadmium (Cd) were recorded on the industrial side while Lead (Pb), Nickle (Ni), and Iron (Fe) were recorded on beach side. While maximum concentration of Manganese (Mn) was observed from civilian side (Kelepertzis, 2014).

Notably, chromium and cadmium from all studied sites exceeds the EPA standard values of Seawater limits which is 200 µg/L for chromium and 10 µg/L for cadmium. While Zn from all sites is less than standard value given by EPA/ or WHO which is 3000 µg/L. While Nickle and Iron from water samples of all sites is less than <0.1

The assessment of surface water quality reveals significant contamination in all zones, with chromium (Cr) and cadmium (Cd) exceeding EPA standard values for seawater. The study emphasizes the influence of anthropogenic activities, especially industrial and agricultural practices, on surface water pollution.

Conclusion

In this study, samples of soil and water from the Libyan Sea coastline were collected to determine the concentrations of heavy metals. Chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn), and iron (Fe) concentrations were assessed in sand, soil, and water samples collected from residential, commercial, and industrial sectors. While soil samples were collected at various distances from the beach, sand samples were taken at various depths. Additionally, water samples were collected at various distances. Notable findings were shown by the results. At a depth of 30 cm, the sand samples from the industrial region had significantly greater chromium contents than those from other sites. At 30 cm depth, cadmium was predominant in samples of commercial sand, and manganese was present in both industrial and residential zones. Chromium was the most prominent metal in soil samples at 20 and 50 cm depths, followed by manganese.

Significant chromium concentrations were identified in water samples, especially in industrial regions; levels were higher the further away from the beach you were. While other heavy metals remained at relatively low levels, water samples showed noticeable amounts of copper, cadmium, and zinc. Overall, this study clarifies how heavy metals are distributed along the Libyan Sea shore, highlighting the presence of chromium, cadmium, and manganese in several samples taken from varied locations and depths.

Overall, the study underscores the importance of sediments as reservoirs for heavy metals in marine ecosystems, emphasizing the potential risks to aquatic organisms and human health through the consumption of contaminated seafood. The discussion on polycyclic aromatic hydrocarbons (PAHs) further adds to the understanding of the environmental challenges faced by Libya, including water scarcity and heightened salinity in coastal aquifers. The study not only contributes valuable insights into the specific context of Libya but also highlights the broader importance of responsible environmental management and regulatory oversight to address and mitigate the impact of anthropogenic activities on coastal ecosystems.

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