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# Evaluation of Heavy Metal Contamination in Water and Sediments of the Gulf of Tobruk, Eastern Libya: Implications for Human Health

***Mohamed Masoud[1] and Eisa S Omar[2]***

[1] *Department of Natural Resources, University of Tobruk, Tobruk, Libya*

[2]*Department of Microbiology, University of Tobruk, Tobruk, Libya*

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**A B S T R A C T**

Globally, contaminated water and sediment provide serious threats to human health and the environment. Aquatic ecosystems and sediments are impacted by pollutants that enter water bodies through municipal wastewater, industrial effluents, and agricultural runoff. Bioaccumulation and biomagnification result from the accumulation of heavy metals, herbicides, and industrial pollutants in sediments. Carcinogenic, neurotoxic, and reproductive effects are caused by human exposure by ingesting, inhalation, and skin contact. Eight samples were taken from four significant locations in the Gulf of Tobruk to assess the level of pollution in the area: four surface water samples and four sediment samples. Specific of the heavy metals, including Fe, Mn, Zn, Ni, Pb, and Cd, had their concentrations measured. The results showed that Zinc, iron, and cadmium levels in water were high, and all heavy elements—Fe, Mn, Zn, Ni, Pb, and Cd—were above the WHO allowable limit in both surface water and sediments. This provides an indication that the Gulf of Tobruk is totally contaminated, unsuitable for a variety of activity uses, and hazardous to human health.

## 1.Introduction:

Domestic and municipal sewage systems are currently one of the biggest problems with the disposal of liquid waste worldwide. A septic tank is frequently used to regulate household sewage, allowing solids to settle out and clear effluents to be gradually released into the nearby regolith. This garbage contains radioactive, explosive, corrosive, toxic, poisonous, or carcinogenic elements that are harmful to both humans and wildlife. Because of their toxicity, durability, and bioaccumulation properties, they represent a major risk to live things, human health, and natural ecosystems (DeForest et all., 2007). The 13 metals in the USEPA's list of hazardous heavy metals are arsenic, antimony, chromium, cadmium, beryllium, lead, copper, zinc, selenium, mercury, nickel, thallium, and silver (Ramos et al. 2002; Salman et al. 2015). Discovered that Tobruk Bay's seawater was highly contaminated. Over time, exposure to these discharges and lack of treatment will result in hazardous levels that impact marine life. (Jalgaif et al. 2018). Tobruk Bay's shoreline area is considered as one of the bays where human activity is most prevalent. Intense urbanisation and remarkable population expansion have resulted in a significant increase in discharges and a broad variety of pollutants that have negative environmental effects. (Masoud 2020). samples gathered from seven sites around Tobruk Bay. The World Health Organization's 2011 permitted levels for chemical parameters and heavy metals were compared to the average concentrations. The findings shown that the average chemical parameter concentrations across all sites exceeded the WHO's allowable limits. (Masoud et *al.,* 2021). The findings of the heavy metals study indicate that the levels of Fe, Mn, Zn, Cd, and Pb exceed the permissible limits. The health of those who participate in some sea sports activities is negatively impacted. Therefore, Tobruk Bay has been classified as contaminated. (Masoud et *al.,* 2022). The accumulation of oil leakage from oil tankers and household garbage, especially heavy metals, in the sediments along the shore of Tobruk Bay is the cause of the deformation of the foraminiferal according to this study. (El-Ekhfifi et al., 2022).

Lead (Pb), derived from the Latin term "Plumbum," is a heavy metal that has been utilized by humans for millennia due to its unique properties, including malleability, resistance to corrosion, and low melting point. Historically, lead has found applications in various industries, including plumbing, paint manufacturing, and battery production. However, the recognition of lead as a potent neurotoxin and environmental pollutant has grown significantly over the past few decades, leading to increased scrutiny and regulation of its use (World Health Organization [WHO], 2019) Nickel (Ni) is a transition metal that is widely used in various industrial applications, including the production of stainless steel, batteries, and alloys. While nickel is an essential trace element required for certain biological processes, excessive exposure can lead to adverse health effects in humans. Nickel exposure primarily occurs through inhalation of contaminated air, ingestion of nickel-containing food and water, and dermal contact with nickel-containing products, such as jewelry and coins (Nordberg et al., 2018).

Zinc (Zn) is an essential trace element that plays a crucial role in numerous biological processes in the human body. It is involved in enzymatic reactions, protein synthesis, immune function, and DNA synthesis. Approximately 300 enzymes require zinc as a cofactor, highlighting its importance in metabolic processes (Prasad, 2013). Given its vital roles, adequate zinc levels are necessary for maintaining overall health and well-being. Iron (Fe) is an essential trace element that plays a pivotal role in various physiological processes in the human body. It is a crucial component of hemoglobin, the protein responsible for oxygen transport in red blood cells, and myoglobin, which facilitates oxygen storage in muscles. Iron is also involved in numerous enzymatic reactions, including those critical for energy production, DNA synthesis, and the metabolism of neurotransmitters (Beard, 2001).

Manganese (Mn) is an essential trace element that plays a critical role in various biological processes in the human body. It is involved in the metabolism of carbohydrates, amino acids, and cholesterol, and it acts as a cofactor for several important enzymes, including manganese superoxide dismutase, which is vital for antioxidant defense (Aschner Aschner, 2005). Manganese is also important for bone formation, wound healing, and the synthesis of connective tissue (Youdim et al., 2004).

Cadmium (Cd) is a heavy metal that is widely recognized as a toxic environmental pollutant. It is released into the environment through various anthropogenic activities, including industrial processes, mining, and the use of cadmium-containing products such as batteries and pigments. Exposure to cadmium can occur through inhalation, ingestion, or dermal contact, leading to significant health risks for humans (Nordberg et al., 2018).

## 2. Materials and methods:

### 2.1 Study area

Tobruk Gulf is located in the center of the city of Tobruk (Fig. 1) and is roughly 5 km long, with a width that ranges from 2 km at the entrance to 0.6 km at the end. The bay's water depths vary from 5 to 16 meters. The primary focus of the current section was the impact of industrial and urban pollution on humanity.

### 2.2 Samples collections

From the Gulf of Tobruk, eight samples were gathered and divided into two sections. In the first section, four samples were taken from the water within the Gulf and four samples were taken from the sediments along the Gulf's beach.

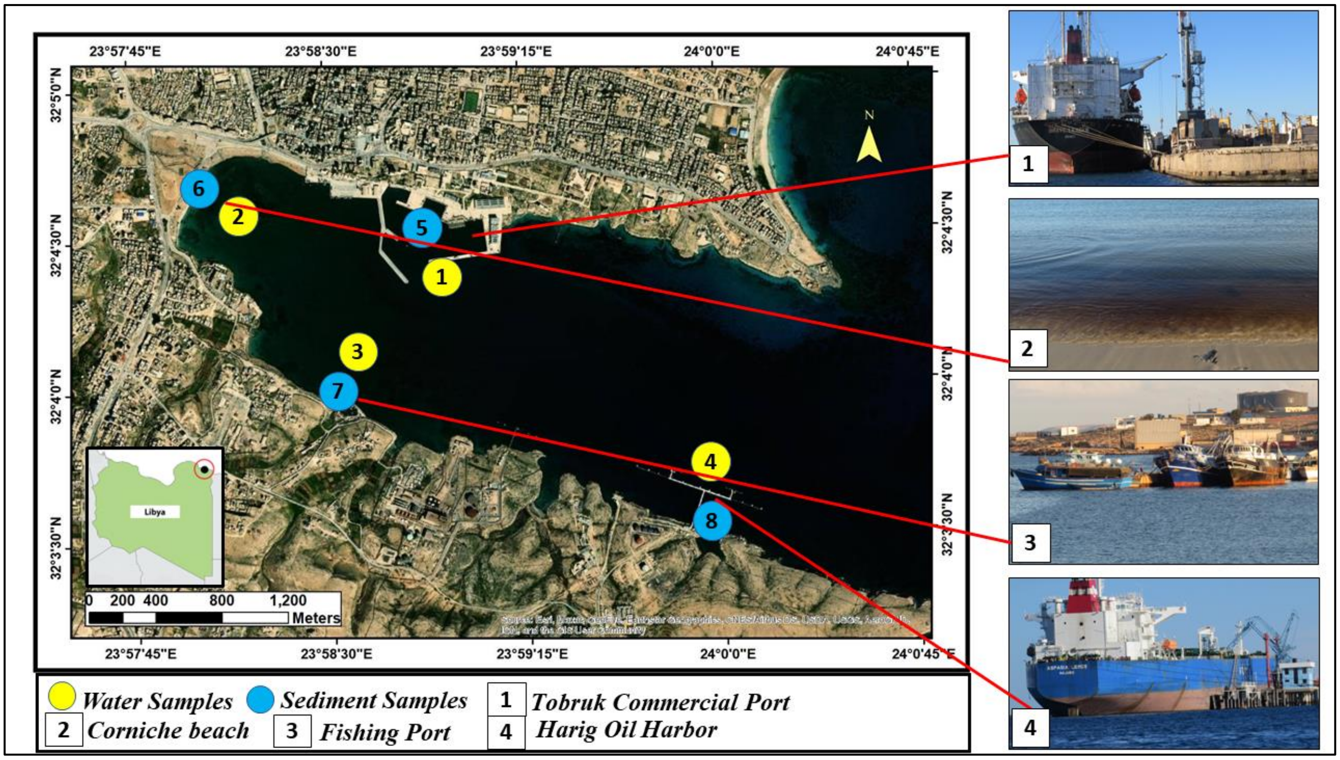


**Fig1. Distribution of sampling sites in Tobruk gulf**

Tobruk Bay was the primary location for the collection of four water samples. Using a Nelson tube, the water samples were collected approximately one metre below the surface of the sea. Using an atomic absorption spectrophotometer, the amounts of the heavy metals Fe, Mn, Zn, Ni, Pb, and Cd were measured. A professional diver was used to collect sediments samples from the chosen locations, which were then frozen until analysis. Sediment samples for total heavy metals were allowed to defrost before being mechanically sieved through a 2 mm sieve and air-dried at 30°C in a circulating oven. Using the Ackwerth and Würfels (1994) approach, 1 gm of sieved sediment was digested by repeatedly adding hydrogen peroxide and nitric acid to completely dissolve all of the sediment's constituent elements. The digested product was heated until its volume decreased, and it was then diluted until it reached a final volume of 100 ml. The atomic absorption spectrophotometer (AAS) was used to identify the elements of concern in the samples, which were Fe, Mn, Zn, Ni, Pb, and Cd.

## 3.Result and Discussion

Seawater samples collected from four locations in the Tobruk Gulf were examined for Fe, Mn, Zn, Ni, Pb, and Cd levels. The results are listed in Table (1).

**Table (1):** Concentration of heavy metals in seawater at Tobruk bay.

| S. n | Stations | Zn gm/l | Fe gm/l | Ni gm/l | Pb gm/l | Mn gm/l | Cd gm/l |
|---|---|---|---|---|---|---|---|
| 1 | *Tobruk Commercial Port* | 0.31 | 1.02 | 18.61 | 3.20 | 1.22 | 0.15 |
| 2 | *Corniche beach* | 0.35 | 1.50 | 15.92 | 5.29 | 1.85 | 0.19 |
| 3 | *Fishing Port* | 0.27 | 0.57 | 20.21 | 4.30 | 4.23 | 1.20 |
| 4 | *Harig Oil Harbor* | 0.18 | 0.52 | 16.30 | 2.53 | 2.50 | 0.15 |
| Average (present study) | | 0.2775 | 0.9025 | 17.76 | 3.83 | 2.45 | 0.4225 |
| Masoud 2020 | | 0.19 | 0.595 | 23.880 | 4.916 | 1.206 | 0.0488 |
| Perm. limits WHO (2011) | | 0.5 | 0.3 | 0.07 | 0.01 | 0.1 | 0.003 |

**Table (2):** Concentration of heavy metals in Sediment at Tobruk bay

| S. n | Stations | Zn gm/l | Fe gm/l | Ni gm/l | Pb gm/l | Mn gm/l | Cd gm/l |
|---|---|---|---|---|---|---|---|
| 5 | *Tobruk Commercial Port* | 25.30 | 52.33 | 1.02 | 0.22 | 24.35 | 0.024 |
| 6 | *Corniche beach* | 27.22 | 55.21 | 1.99 | 0.29 | 21.65 | 0.044 |
| 7 | *Fishing Port* | 32.62 | 58.60 | 1.80 | 0.28 | 25.29 | 0.041 |
| 8 | *Harig Oil Harbor* | 23.20 | 51.80 | 1.01 | 0.21 | 23.33 | 0.012 |
| Average (present study) | | 27.085 | 54.485 | 1.455 | 0.25 | 23.655 | 0.03025 |
| (Masoud et *al.*, 2022). | | 27.02 | 55.249 | - | 0.2165 | 26.541 | 0.0138 |

**1.Zinc (Zn):**

In **Water samples**: Zinc concentrations are given in Table (1) and illustrated in Fig. (2). The growth of aquatic organisms depends on zinc. waste from homes is thought to be the primary source of zinc. According to James (1991). Zinc content ranges from 0.18 to 0.35 gm/l with an average of 0.277 gm/l, which is generally higher than those recorded in Masoud 2020 and the permissible limits given by WHO (2011). (Not exceed 0.50 gm/l). The lowest content of Zn (0.18 gm/l) recorded In Harig Oil Harbor location which is lower than Masoud2020, Whereas The highest Zinc content (0.35 gm/l) is recorded at station no.2 (Corniche beach) Because the area receives sewage directly without any treatment, a high percentage of zinc is typical in this station.

In **Sediments samples:** Zinc concentrations fluctuate between 23.20 and 32.62 gm/l with an average of 27.085 gm/l which is equal average (**Masoud et *al.*, 2022)** and the permissible limits given by WHO (2011). Given in Table (2) and illustrated in Fig. (3). The highest Zinc content in sediments samples in area is recorded at Samples no.7 (Fishing Port) .excessive zinc intake can also have detrimental effects on human health. High levels of zinc can lead to toxicity, presenting symptoms such as nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches (López et al., 2016). Chronic exposure to elevated zinc levels may interfere with the absorption of other essential minerals, such as copper and iron, potentially leading to secondary deficiencies (Hughes et al., 2013). The sources of zinc in the diet include meat, shellfish, legumes, seeds, nuts, dairy products, and whole grains. The bioavailability of zinc varies depending on the food source; animal-based foods generally provide more readily absorbable forms of zinc compared to plant-based sources due to the presence of phytates that inhibit absorption (Hotz Gibson, 2001).

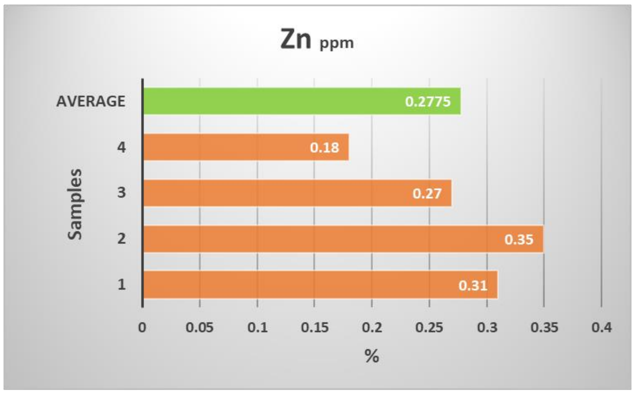


**Fig. (2):** Zn concentrations in Tobruk bay seawater.

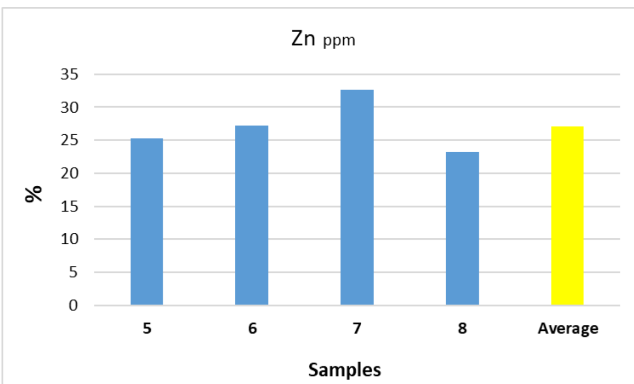


**Fig. (3):** Zn concentrations in Tobruk bay Sediment.

**2.Iron (Fe):**

Iron concentrations fluctuate between 0.52 and 1.50 gm/l with an average of 0.902 gm/l, generally higher A past investigation by Masoud 2020. (Table 1). In addition, Fe concentrations are higher than the permissible limits of WHO (2011) (not exceed than 0.3 gm/l). The lowest concentration of Fe is documented in Two stations Fishing Port (0.57 gm/l) and Harig Oil Harbor (0.52 gm/l) which is similar to Masoud's 2020 results. The highest Fe concentration was recorded at station 2 (Fig. 4) where the bay receives massive discharges of household sewage. In **Sediments samples:** Iron concentrations content ranges from 51.80 to 58.60 gm/l with an average of 54.485 gm/l, which is generally higher than those recorded in (**Masoud et *al*., 2022)** and the permissible limits given by WHO (2011). ((not exceed than 0.3 gm/l). While Fishing Port station has Fe value 58.620 gm/l higher than all stations in the study area. Fig (5). excessive iron accumulation in the body can lead to a condition known as hemochromatosis, which can cause damage to organs such as the liver, heart, and pancreas (Bacon et al., 2001). This condition often results from genetic predisposition but can also be exacerbated by high dietary iron intake or frequent blood transfusions. The balance of iron homeostasis is tightly regulated by the body through mechanisms involving absorption, storage, and recycling of iron to prevent both deficiency and toxicity (Andrews,2000). Dietary sources of iron are categorized into two forms: heme and non-heme iron. Heme iron, found in animal products such as red meat and poultry, is more readily absorbed than non-heme iron, which is present in plant-based foods like legumes, grains, and leafy greens (Hurrell Egli, 2010). The bioavailability of non-heme iron can be influenced by various dietary factors, including the presence of enhancers like vitamin C and inhibitors such as phytates and polyphenols

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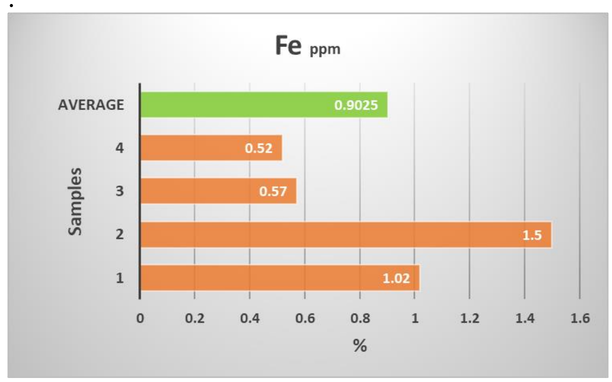


**Fig. (4):** Fe concentrations in Tobruk bay seawater.

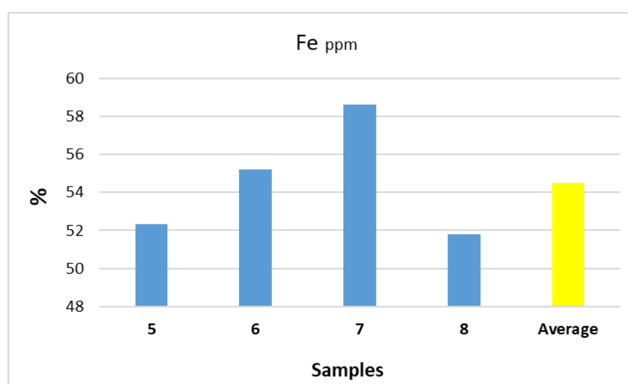


**Fig. (5):** Fe concentrations in Tobruk bay Sediment.

**3. Nickel (Ni)**

Fig. (6) shows the distribution of Ni content. With an average of 17.66 gm/l, it varies between 15.92 gm/l and 20.21 gm/l. which is generally higher than the permissible limits of WHO (2011) for drinking water and lower than Masoud 2020. While Fishing Port station has Ni value 20.21 gm/l higher than the permissible limits of WHO (2011). It is expected that this area will be contaminated and used for painting and boat repair. Ni is always exploited to improve oil (Helal et al., 1984). The distribution of Ni concentration in sediments is displayed in Fig. (7). It ranges from 1.01 gm/l to 1.99 gm/l, with an average of 1.455 gm/l. This is typically greater than the WHO (2011) drinking water permitted levels. However, the Ni result of 1.99 gm/l at Corniche Beach Station is higher than the WHO's (2011) permissible levels This is due to the reason that this area receives more direct sewage, industrial pollutants, and home garbage than other stations. The health effects of nickel are diverse and can affect multiple organ systems. The most well-documented adverse effects are related to respiratory health, particularly in occupational settings where inhalation of nickel dust or fumes is common. Nickel exposure has been associated with respiratory diseases, including asthma, chronic bronchitis, and lung cancer (IARC, 2012). Furthermore, nickel is known to be a potent allergen; nickel allergy is one of the most common forms of contact dermatitis, affecting a significant portion of the population (Sampogna et al., 2017) In addition to respiratory and dermatological effects, nickel exposure can also have systemic health implications. Studies have suggested that prolonged exposure to high levels of nickel may lead to cardiovascular issues, renal dysfunction, and potential reproductive toxicity (Baker et al., 2018). The mechanisms underlying nickel toxicity are complex and involve oxidative stress, inflammation, and disruption of cellular signaling pathways (Meyer et al., 2016)

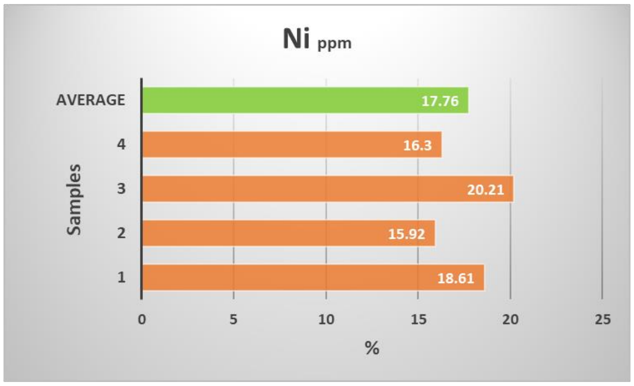


**Fig. (6): Ni** concentrations in Tobruk bay seawater.

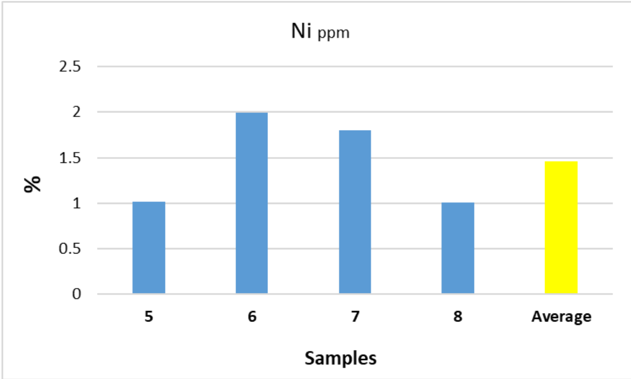


**Fig. (7): Ni** concentrations in Tobruk bay Sediment.

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**4.Lead (Pb)**

It is evident from the result of table (1) and figure (8) that the concentration of Pb ranged from 2.53 gm/l to 5.29 gm/l. with an average of 3. 83 gm/l. which appears higher than the WHO2011and the lowest than the average given in Masoud 2020. The maximum Lead content was recorded at sewage discharge tube in station (2), However the lowest concentration of **Pb** (2.35 gm/l) is exhibited by station no. 4 (Harig Oil Harbor). Table (2) and Figure (9) clearly show that the Pb concentration in sediments ranged from 0.21 to 0.29 gm/l, with an average of 025 gm/l. This is higher than the WHO 2011 average and lower than the average reported in Masoud 2022. Station number 4 (Harig Oil Harbour) has the lowest Pb concentration (0.21 gm/l), whereas station (2)'s sewage discharge tube had the highest lead content. Lead exposure can occur through multiple pathways, including ingestion of lead-contaminated food or water, inhalation of lead dust, and dermal contact with lead-containing products. The most vulnerable populations are often children and pregnant women, as lead can have devastating effects on neurological development and fetal health (Centers for Disease Control and Prevention [CDC], 2021). Once absorbed into the body, lead can accumulate in bones, teeth, and soft tissues, leading to chronic health issues. The health effects of lead exposure are extensive and multifaceted. Lead is known to adversely affect the central nervous system, resulting in cognitive impairments, behavioral problems, and developmental delays in children (Lanphear et al., 2005). In adults, lead exposure is associated with increased risks of hypertension, cardiovascular diseases, renal dysfunction, and reproductive issues (Navas-Acien et al., 2007). Notably, even low levels of lead exposure have been linked to significant health risks, emphasizing the need for comprehensive public health strategies aimed at reducing lead exposure in at-risk populations (WHO, 2019).

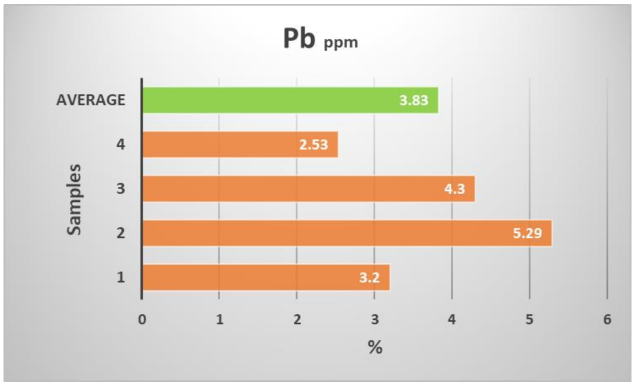


**Fig. (8): Pb** concentrations in Tobruk bay seawater.

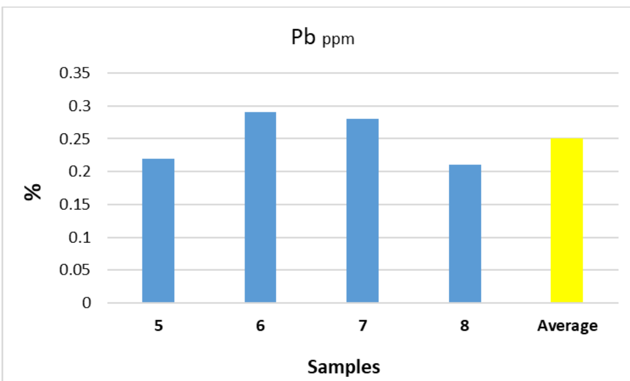


**Fig. (9): Pb** concentrations in Tobruk bay Sediment.

**5. Manganese (Mn):**

Manganese concentrations fluctuate between 1.22 and 4.23 gm/l with an average of 2.45 gm/l, generally lower than Masoud2020 and higher than the permissible limits of WHO (2011) (not exceed 0.1 gm/l) Table (1). The lowest concentration of Mn is documented in Two locations Tobruk Commercial Port (1.22 gm/l) Corniche beach (1.85 gm/l) Whereas Highest **Mn** concentration (4.23 gm/l) was recorded at station 3(Fishing Port). Figure (10). Manganese concentrations in sediments range from 21.65 to 25.29 gm/l, with an average of 23.65 gm/l. These amounts are usually lower than Masoud2022 and higher than the WHO (2011) allowed limits (not to exceed 0.1 gm/l). Table (2). Corniche Beach station had the lowest Mn concentration (21.65 gm/l), while station 3 (Fishing Port) had the highest Mn concentration (25.29 gm/l). Figure 11. Despite its essentiality, manganese can be toxic at elevated levels. Chronic exposure to high levels of manganese, particularly in occupational settings such as mining and welding, can lead to a neurological disorder known as manganism, which resembles Parkinson's disease (Racette et al., 2001). Symptoms of manganism include tremors, rigidity, and impaired motor function, highlighting the delicate balance between the beneficial and harmful effects of manganese in the body. Dietary sources of manganese include nuts, seeds, whole grains, legumes, and leafy green vegetables. The bioavailability of manganese from these sources can be influenced by dietary factors such as phytates and other components that may inhibit its absorption (Baker Franke, 2003). The Recommended Dietary Allowance (RDA) for manganese varies by age and sex; however, most individuals can meet their manganese needs through a balanced diet without supplementation (Institute of Medicine, 2001)

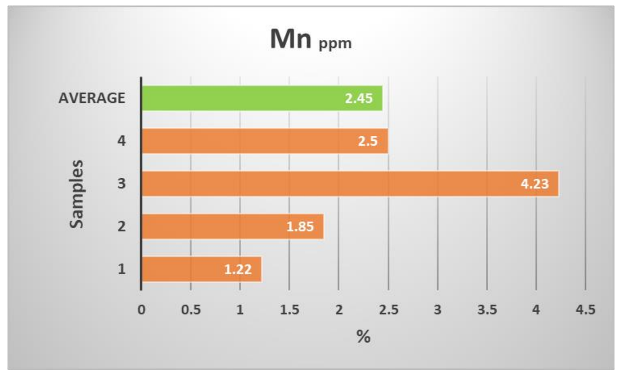


**Fig. (10): Mn** concentrations in Tobruk bay seawater.

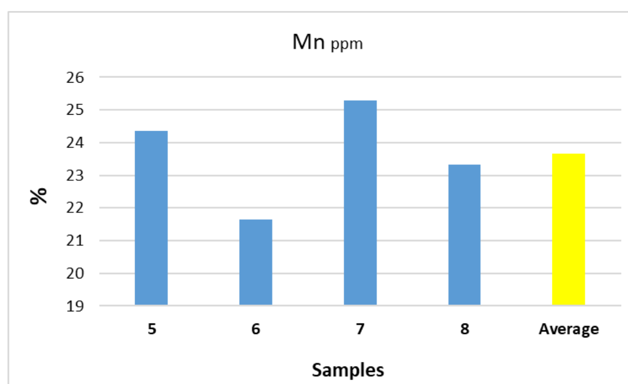


**Fig. (11): Mn** concentrations in Tobruk bay Sediment.

**6. Cadmium (Cd)**

Cadmium is extremely harmful to biota and living organisms, even at low doses, and has a long biological life of 20 to 30 years in the kidney (Green et al., 1986).

The distribution of Cd content is shown in Fig. (12). Cd averages 0.4225 gm/l, with variations between 0.15 and 1.20 gm/l. Fishing Port No. 3 has the highest concentration of Cd (1.20 gm/l), while Stations Nos. 1 and 4 have the lowest concentration (0.15 gm/l). The levels of Cd in Tobruk seawater are higher than those found in Masoud2020 as well as the WHO's (2011) permissible limits, which are not to exceed 0.003 gm/l. Therefore, in addition to Pb, Cd is regarded as a polluting metal in Tobruk Bay water. Figure 13 illustrates the growth of Cd concentration in sediments. The average concentration of CD is 0.03025 gm/l, with fluctuations that vary from 0.12 to 0.044 gm/l. Stations No. 1 and 4 had the lowest concentrations of Cd, while Corniche beach No. 2 has the highest value (0.44 gm/l). Compared to Masoud2022, Tobruk seawater has a higher concentration of Cd.The human body does not have a known physiological requirement for cadmium, and its presence can lead to detrimental health effects. Cadmium has been linked to a variety of adverse health outcomes, particularly affecting the kidneys, lungs, and bones. Chronic exposure to cadmium is associated with kidney dysfunction, characterized by proteinuria and impaired renal function (Järup, 2003). The metal accumulates in the kidneys over time, leading to nephrotoxicity and potential renal failure (Satarug et al., 2003) In addition to renal effects, cadmium exposure has been implicated in respiratory diseases. Inhalation of cadmium fumes or dust can cause lung inflammation and damage, resulting in conditions such as chronic obstructive pulmonary disease (COPD) and lung cancer (López-Carrillo et al., 2004). Furthermore, cadmium is recognized as a carcinogen, with evidence suggesting an increased risk of prostate, lung, and kidney cancers among individuals with elevated cadmium exposure (Boffetta et al., 2004)

Cadmium also poses risks to bone health. Studies have shown that long-term exposure can lead to osteoporosis and an increased risk of fractures due to its interference with calcium metabolism and bone mineralization (Kido et al., 2004). This effect is particularly concerning for vulnerable populations such as the elderly, who may already be at risk for bone-related diseases
cadmium-rich soils or irrigated with contaminated water. Shellfish, liver, and certain leafy vegetables are known to accumulate cadmium, posing additional risks for dietary exposure (Satarug Moore, 2004). Public health measures aimed at reducing cadmium exposure include monitoring environmental levels, regulating industrial emissions, and educating the public about potential sources of exposure.

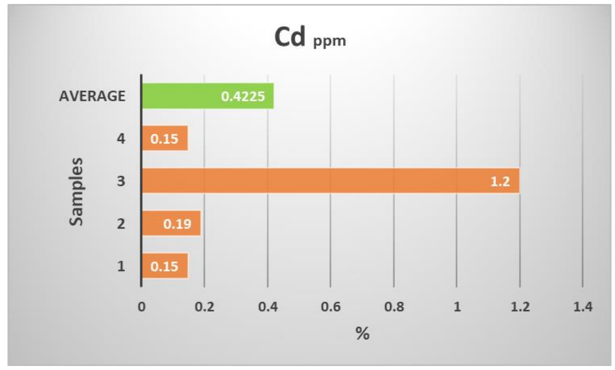


**Fig. (12): Cd** concentrations in Tobruk bay seawater.

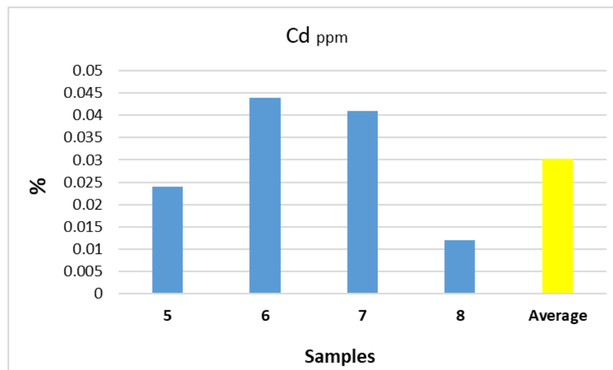


**Fig. (13): Cd** concentrations in Tobruk bay Sediment.

## 4. CONCLUSIONS:

In this study found that contaminated water and sediment provide serious threats to human health and the environment. Aquatic ecosystems and sediments are impacted by pollutants that enter water bodies through municipal wastewater, industrial effluents, and agricultural runoff. Bioaccumulation and biomagnification result from the accumulation of heavy metals, herbicides, and industrial pollutants in sediments. Carcinogenic, neurotoxic, and reproductive effects. Also, It was found that cadmium is the most dangerous substance to human life, and it is present in samples and increases over time, so the following recommendations must be taken into account.

## 5. Recommendation:

1. Reducing chemical use: Less chemical pollution of water supplies results from reduced use of pesticides and fertilizers in agriculture.

2. Developing the sanitation infrastructure: Putting in place and improving effective sanitation systems helps prevent waste from leaking into water sources.

3.The prevention of hazardous materials from seeping into the Tobruk Gulf facilitated by recycling and proper waste disposal.

4. Reducing plastic: Reducing plastic pollution in the sea is facilitated by reducing the use of plastic bottles and bags.

5. Raising public understanding of environmental issues: Pollution can be reduced by educating people about the need of preserving clean water.

Understanding the complex interactions between water and sediment contamination is crucial for developing sustainable management practices and protecting human health and environmental quality.

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**Conflict of interest**: The authors declare that there are no conflicts of interest

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