

Risk Assessment of Heavy Metals in the Drinking Water Source and Marine Benthic from Tobruk Coastline (Case Study : The Port and Gulf of Tobruk - Libya)

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Abstract – Coastal areas provide several important benefits to human beings in terms of foodstuff resources and ecology amenities. The human beings activities may have significant adverse effects on the ecosystems health and the sustainability of resources. The heavy metal contamination has become a serious problem in the aquatic environment, including marine sediments. The increased exposure of Tobruk port to liquid waste coming from the ground, oil change stations and marine barges carrying crude oil to and from this city may make it one of the most polluted areas as a result of this negative impact. Liquid waste is one of the main sources of heavy metal pollutants. Tobruk f harbour is one of the most polluted areas due to the adverse effect of effluents from land-based sources. The aim of this study was analyzing the content of heavy metals in seawater, then assessing and evaluating the level of heavy metal contamination its ecological risks. The present study investigated the concentrations of K, Na, and Cd in seawater of Tobruk fishing harbour and surrounding area. The study also identified the major properties of the seawater PH. fifteen sampling stations were selected to conduct the study in Tobruk harbour surrounding area. The samples were taken from the study stations at month from September of 2021 . The samples were taken in September. All metals were determined and analyzed by Flame Atomic Absorption Spectrophotometer in for Cd, and for Na and K were determined by using JENWAY Flame Photometer PFP7 modeled in laboratory of Tobruk – Libya.

Key words: Heavy Metals, Spectrophotometer, Tobruk port.

1. Introduction:

1.1. Background

Heavy metal pollution is a serious problem that occurs in sea waters. Heavy metal pollution caused disorder in humans, ecosystems and organisms as well as a decrease in the quality of sea waters. Declining in sea water quality can be caused by contaminants such as heavy metals with a high concentration of highly impact to the aquatic environment, especially living organisms (Siaka, 2008). The entry of contaminants into the environment due to human and natural activities is one of the most important issues facing today's communities. Due to the industrial and economic growth and the production of a variety of compounds and chemicals followed by increased consumption man makes some unwanted pollutants, many of which cause serious problems and risks for the environment and for man himself. (Kim, K.T et al., 2011).

The Gulf of Tobruk is a sea open to untreated sewage, runoff, abattoir wastewater, and leachate of solid wastes around it. Regarding the above-mentioned issues and due to the fact that it is a place for the migration of birds in cold seasons as well as for public promenade, swimming, and fishing the present study was thus carried out to investigate the concentration of heavy metals such as lead, cadmium, sodium, potassium and calcium, and due to the discharge of sewage of the city in the gulf. The pollution entail disruption of the natural condition of the environment by human activity. Both terms are different by the harshness of the consequence: pollution makes the loss of possible resources (Goldberg 1992). In the marine environment, human-made instabilities take many forms. Due to the source strengths and paths, the extreme impacts incline to be in the coastal area. Waters and sediments in such areas tolerate the prominent flow of industrial and sewage discharges and are a matter to indulge dumping (Hester and Harisson 2000).

The fishing port of the Gulf of Tobruk and the surrounding coastal environment face significant and serious threats from land-based sources of pollution. The small Gulf of Tobruk is witnessing a rapid increase in population as it already numbers around 200,000 people (Libyan Central Bureau of Statistics, 2021). The limited land resources, the physical isolation of the area and the backward environmental management system have caused various serious problems. These problems It leads to pollution of the fishing port, coastal area and sea water as well as marine sediments, deterioration of natural resources and natural habitats, and a decrease in fish populations. The fisheries and tourism sectors are under direct threat due to many negative impacts (MENA, 2001). The quality of sea water and sediment in the fishing port along the coast of the Gulf of Tobruk in the Mediterranean is highly polluted from untreated sewage of more than 90,000 m³/day sewage discharge point (September, 2020). The introduction of sewage into the sea causes a number of degradation effects on aquatic life ; Including phytoplankton, zooplankton, crustaceans, macroalga and fish species. The main causes of these disturbances are: degradable organic matter, refractory organic matter, dissolved

organic matter, heavy metals, suspended solids, pathogens, nutrients, pesticides, and pesticides used extensively in agriculture and some small industries (MENA, 2001).

Sediments are an imperative basin of assortment of contaminants, predominantly heavy metals and may attend as a supplemented source for benthic organisms (Wang et al., 2007) particularly in estuarine ecosystems. Metals may be existing in the estuarine ecosystem as dissolved kinds, as free ions or materializing organic complexes with humic and fulvic acids. Additionally, many metals for example, Lead associate freely with particulates and become adsorbed or co-precipitated with carbonates, oxyhydroxides, sulphides and clay minerals. Accordingly, sediments accumulate contaminants and may deed as long-term stores for metals in the environment (Spencer and MacLeod, 2002). The incidence of higher concentrations of metals in sediments observed at the nethermost of the water column can be a significant indicator of man-induced pollution rather than natural enrichment of the sediment by environmental weathering (Davies et al., 1991). The analyses of marine water or sediment samples still are subject to a range of limitations, in that the methods do not allow for the estimation of the quantity of the metal which is biologically available (Etim et al., 2013).

However, dissolved substances in seawater along the Gulf of Tobruk and the fishing port pose a threat not only to the marine ecosystem but also to groundwater quality and may be dangerous to humans by causing unpredictable human disease. Thus, the food chain of the marine ecosystem in Tobruk is strongly influenced by the above factors. Few short-term studies have been conducted to monitor and assess seawater and terrestrial soil quality along the Gulf of Tobruk especially the distribution of heavy metals. This study was conducted due to the lack of detailed pollution monitoring and assessment programs regarding heavy metal pollution in the vicinity of the Gulf of Tobruk. The current concentrations of heavy metals, types of heavy metals and the presence of various elements that may be present in the existing sediments entering the Gulf of Tobruk for fishing are unknown. Hence, there is a need to monitor and evaluate heavy metals in sea water, marine sediments and fish species in the vicinity of the fishing port along the Gulf of Tobruk, and to suggest a coastal management strategy to control pollution in the vicinity and the surrounding environment.

1.2. Problem Statement And Justification

The main source of pollution along the coastal waters of Gulf Tobruk is the discharge of untreated wastewater along the coast. The beaches in front of the city of Tobruk are polluted by the discharge of sewage and individual sewage drains that end either on the beach or a short distance from the seashore. The introduction of raw sewage into the sea can cause a number of adverse effects, including, untreated sewage affects marine life and causes a lack of oxygen in seawater, increased turbidity may affect marine organisms, eutrophication (increased concentration of nutrients), potentially harmful algal blooms, bacterial overgrowth, shift in

species composition encouraging abundance of benthic rather than pelagic species and poisoning of species with toxic substances.

Urbanization, industrialization, tourism and shipping (ports) are major factors feared to cause pollution of the marine environment. The Tobruk Corniche is some of the areas along the coast of the Gulf of Tobruk that are at risk of having high levels of heavy metal pollutants due to the activities around them. Through the food chain, heavy metals, including lead, cadmium, zinc, manganese, copper, and mercury in seawater, sediments and fish and other marine animals may affect human health. Untreated sewage estuaries contain both organic and inorganic toxic substances, such as nitrates and heavy metal. The wastewater and polluted seawater containing large amounts of heavy metals and oils also affect the seawater desalination process, as the Gulf of Tobruk is considered the supplier of the Tobruk Seawater Desalination Plant. Therefore, there is a need to evaluate these heavy metals in the port of the Gulf of Tobruk and the surrounding area along the coast of the city of Tobruk. The Gulf of Tobruk also faces the problem of unloading oils from oil tankers at the port of Marsa Al-Hariqa sea oil port.

1. Materials and Methods

2.1. Study Area

Samples of polluted seawater were collected from the coast of the Gulf of Tobruk from several areas within the Gulf the table 2.1 lists geographical latitude and longitude of the sampling locations of the study area. To assess the general concentration level of pollution in the seawater in the coastal environment of Tobruk. The case study area is selected as Tobruk harbor and the surrounding environment in the west, east and south parts of the harbor area. Tobruk fishing harbor is located on the Mediterranean Sea at Tobruk beach.

2.2. The Sampling Collection

To investigate the distribution of heavy metals in the seawater. The samples were collected from the port of Tobruk and the surrounding area, which was taken from several areas. The data was collected from a Gulf of Tobruk, which was divided into thirteen points. As in table 1 above lists and figure 1 shows the location map of the samples that were the location of the study.

Collected from the study area, the standard sample, and a sample of sea water in an area far from pollution, which was considered as a reference sample, and for which a specific code was specified for each of them seawater samples were collected by a grab sample from a distance of 150 m inside the sea (parallel to the shoreline) along the 15 locations during September 2021. The collected samples were immediately transferred to bottles until analysis. Table 1 lists the samples that were collected from the study area, the standard sample, and a sample of sea water in an area far from pollution, which was considered as a reference sample, and for which a

specific code was specified for each of them as in Figure 1 and Figure 2 shows the location map of the study area.

Table 1 lists the samples that were collected from the study area

No.	Sample Code	Sample Location	
		Longitude	Latitude
1	A1	E 23.971035	N 32.079598
2	A3	E 23.97328	N 32.07597
3	A5	E 23.97719	N 32.07029
4	A7, Intake of Tobruk Desalination Station	E 23.98437	N 32.06528
5	B1	E 23.967547	N 32.078826
6	B3	E 23.971086	N 32.075262
7	C1, Before And After injection	-	Tobruk Desalination Station
8	C4, Brine After Desalination	-	Tobruk Desalination Station
9	C5, Drinking Water	-	Tobruk Desalination Station
10	D1	E 23.986842	N 32.064709
11	E Golf company	E 23.998781	N 32.061550
12	F2	E 23.99850	N 32.06762
13	F4	E 24.00805	N 32.06619
14	H0	E 23.976611	N 32.065856
15	Tobruk sea port	E 23.975983	N 32.077212
16	The Reference from wadi alsahal	E 23.835590	N 32.138522



Figure 1: Map shows Tobruk harbor in the Mediterranean Sea

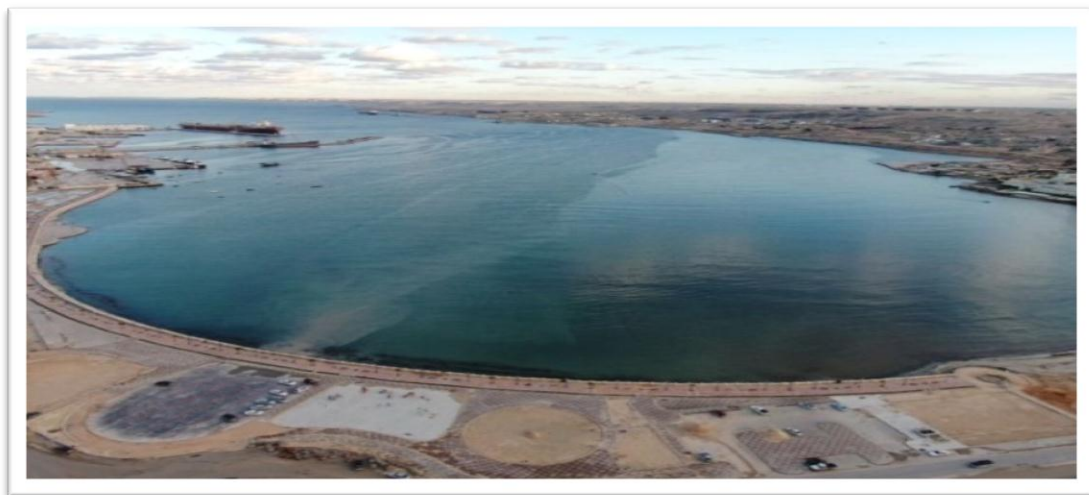


Figure 2: Map shows sampling stations of the study area

2.3. The Sample Preparation And Analysis

2.3.1. The Element Of Potassium And sodium

The concentrations of Na and K in seawater samples were determined by using Jenway flame photometer models PFP7, as shown in figure 3. The standard solution was prepared by dissolving 0.7915 g, KCl and 0.4715g, NaCl in 1L distilled water to produce a solution of 500 ppm K and 250 ppm Na. This solution was used as a stock solution and diluted to prepare std.

solution used in the analysis. By plotting a graph of display reading (intensity) against standards concentrations and then from the sample reading, the concentration of sample can be calculated from the calibration plot.



Figure 3: Shown the Jenway flame photometer models PFP7. Where using to determined concentrations of Na and K in seawater samples.

2.3.2. The Metal Of Cadmium

For cadmium the ICP–MS instrument used the inert argon gas as a plasma source to generate the ionization state for elements; as shown in figure 4. Mass spectrometer (MS) used in parallel with a quadrupole mass filter for separating the produced ions for detection and investigation. Analytes concentration of most elements in the periodic table could be determined at ppb and ppt levels. ICP–MS used for qualitative, isotopes ratio, semi-quantitative analysis, and quantitative analysis. Also, it can determine the ratios of isotopic in liquid samples like water, wastewater, extracts and digested material in a liquid state.



Figure 4: Shown the ICP–MS instrument used the inert argon gas as a plasma source to generate the ionization state for elements of cadmium and lead.

2.4. Results and Discussion

The main source of pollution in the coastal environment of Tobruk is the discharge of untreated sewage along the shoreline. The beaches are polluted by sewage discharges and individual sewage drains, ending either on the beach or at a short distance away from the seashore. The results achieved during this study are discussed in the following sections.

3.1. Distribution Of Heavy Metals And Element In Seawater

Heavy metals are considered to be among the highest serious pollutants of water ecosystems, because of their high possibility to enter and being accumulated in nourishment chain (Tam and Wong, 2000; Erdoğrul and Erbilir, 2007). In definite environmental conditions of marine water systems, heavy metals may be accumulated to level of toxic concentration and cause unusual damage to the ecosystem (Jefferies and Firestone, 1984; Freedman, 1989). The heavy metals pollution sources include the run-off from agricultural and urban areas, discharges from factories and municipal sewer systems, leaching from dumps and former industrial sites, and atmospheric deposition (Singh and Steinnes, 1994; Kumar Singh et al., 2007).

A total of 16 water samples were collected from the Tobruk harbor and surrounding area and analyzed to investigate the concentration levels of heavy metals in the seawater including: K, Na and Cd. The sampling and laboratory analysis were The obtained results of seawater physicochemical parameters are discussed in the following sections and presented in Table 2.

Table 2: Concentrations of analyzed Heavy metals and element in seawater

Locations and Sample Code	Cd, mg/l	K, mg/l	Na, mg/l
A1	0.198	0.828	2.214
A3	0.099	1.089	5.973
A5	0.198	1.197	6.396
A7, Intake of Tobruk Desalination Station	0.088	0.873	6.361
B1	0.033	0.828	6.267
B3	0.066	0.822	6.405
C1, Before And After injection	0.066	0.759	6.357
C4, Brine After Desalination	0.233	0.909	6.966
C5, Drinking Water	0.002	0.002	0.036
D1	0.11	0.693	5.940
E Golf company	0.968	0.714	6.246
F2	0.22	0.771	6.273
F4	0.189	0.846	6.210
H0	1.108	0.741	6.264
Tobruk sea port (TSP)	0.605	0.762	6.567
The Reference from Wadi Alsahal	0.005	0.02	0.02
Standard	0.003	0.635	6.158

3.2. Concentrations Of Cadmium

The average concentration of cadmium in seawater has been assumed about $0.1\mu\text{g/l}$ or less (Yim, et al.,1981 and Owen 2000 and WHO (2001)). reported that current measurements of dissolved cadmium in surface waters of the open oceans gave values of $< 5 \text{ ng/l}$. The vertical distribution of cadmium concentrations in marine waters is described by a surface depletion and shallow water supplementation, which relates to the form of nutrient concentrations in the considered areas (Shen and Boyle, 1987). Such distribution is considered to be the result cadmium which adsorbed by phytoplankton in surface waters and its transportation to the deep water, integration to organic fragments, and consequent releases.

The distribution of cadmium concentrations in water samples collected from Tobruk harbor and surrounding area are shown in Figure.5. The concentration values of Cd in seawater surface are ranged from 0.002 to 1.108 mg/l with a mean value of 0.555 mg/l. The highest concentration values of Cd 1.108 mg/l in seawater were observed at locations H0. The lowest concentration values of Cd 0.002 mg/l in seawater were observed at locations C5 (Seawater after Desalination).

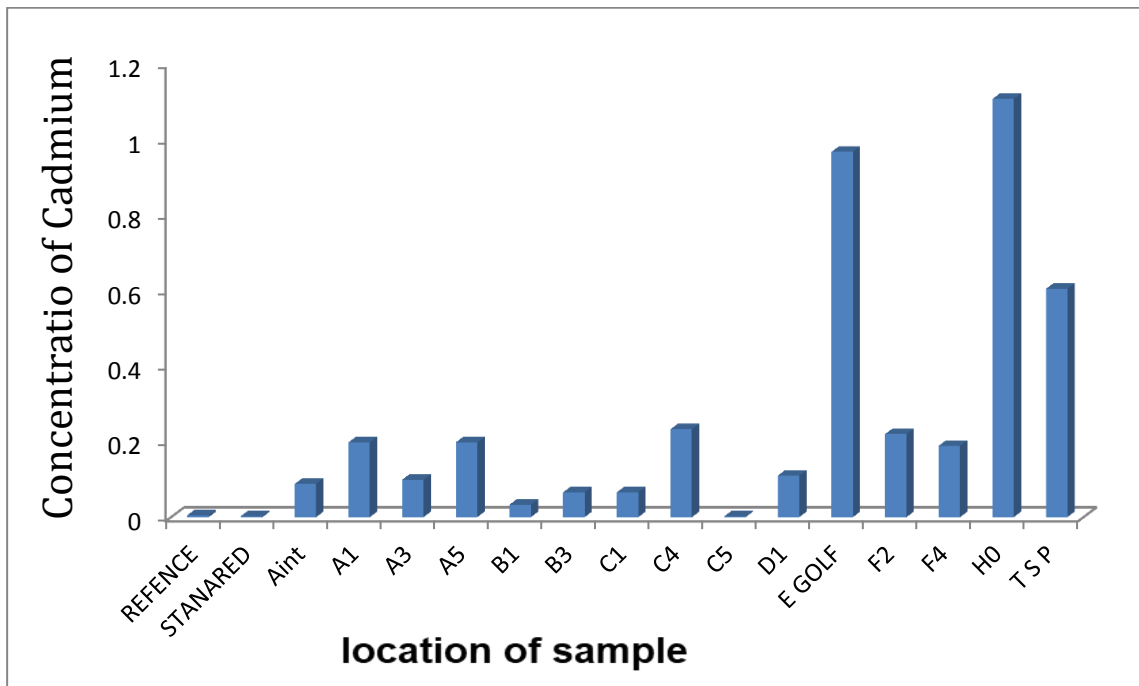


Figure 5: Distribution of Cadmium concentration in the seawater of Tobruk harbor and surrounding area.

3.3. Concentrations Of Potassium

The distribution of Potassium concentrations in water samples collected from Tobruk harbor and surrounding area are shown in Figure 6. The concentration values of K in seawater surface are ranged from 0.002 to 1.197 mg/l with a mean value of 0.600 mg/l. The highest concentration values of K 1.197 mg/l in seawater were observed at locations A5. The lowest concentration values of K 0.002 mg/l in seawater were observed at locations C5 (Seawater after Desalination).

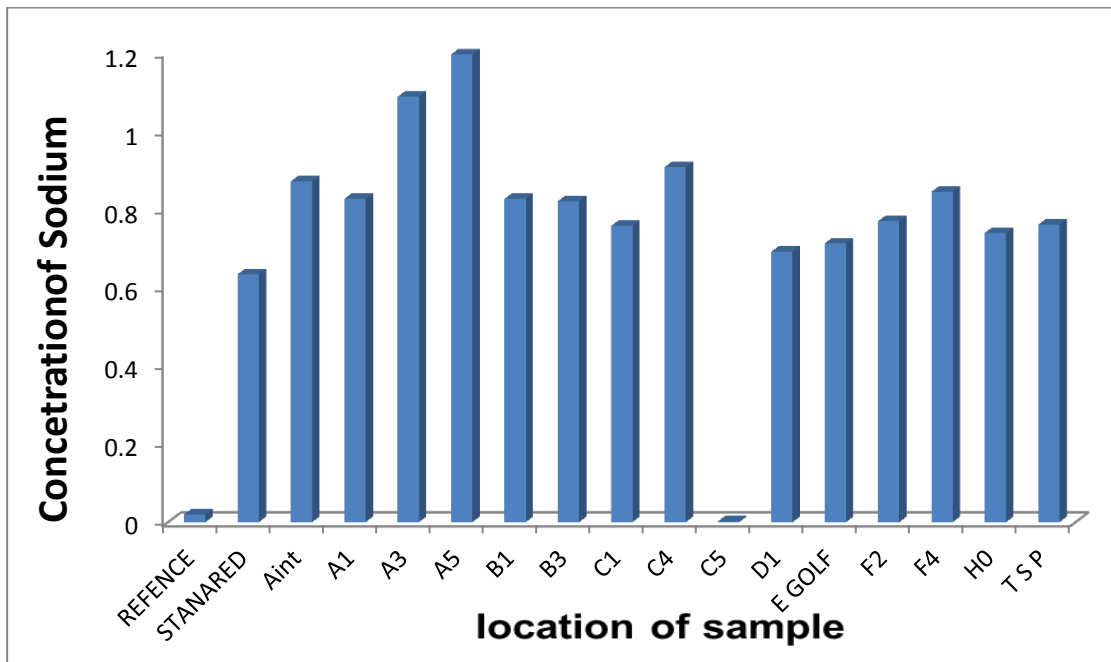


Figure 6: Distribution of potassium concentration in the seawater of Tobruk harbor and surrounding area.

3.4. Concentrations Of Sodium

The distribution of Sodium concentrations in water samples collected from Tobruk harbor and surrounding area are shown in Figure 7. The concentration values of Na in seawater surface are ranged from 0.036 to 6.966 mg/l with a mean value of 3.501 mg/l. The highest concentration values of Na 6.966 mg/l in seawater were observed at locations C4. The lowest concentration values of Na 0.036 mg/l in seawater were observed at locations C5 (Seawater after Desalination).

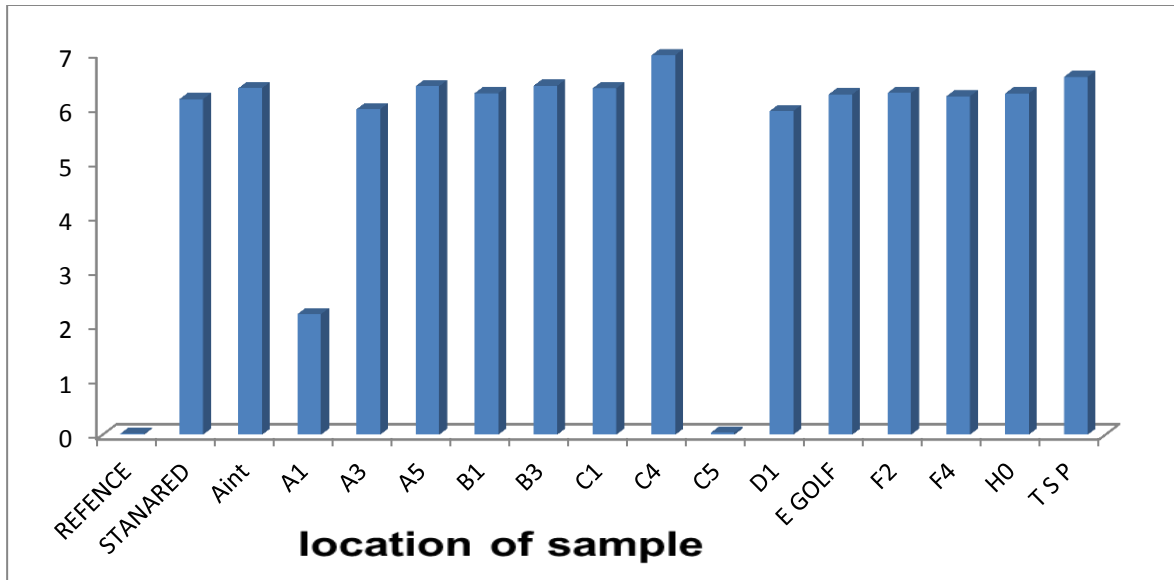


Figure 7: Distribution of sodium concentration in the seawater of Tobruk harbor and surrounding area.

3.5. Contamination Factor Calculation (C_f)

We calculate the pollution coefficient of metals and heavy elements, determined the proportion of each of which in each sample drawn from sea water, dividing the concentration of minerals and reference elements for each sample of pure water samples that taken from a site far from the places of contamination by the concentration of minerals and elements that located. Its value above the standard limits according to the World Health Organization, using the following equation (1)

$$C_{fi} = \left(\frac{C_{Ai}}{C_{Ni}} \right) - 1 \text{ -----(1)}$$

Where :

C_{fi} : Contamination factor

C_{Ai} : analytical concentration

C_{Ni} : Permissible Concentration (upper allowable concentration)

Contamination index calculates the relative contamination of different metals separately and present the sum of generated components as a representative (Helen LE and Othman OC 2014). Contamination index was calculated where all Calculation are shown in Table 3:

Table 3: Contamination factor calculation (Cf) Heavy metals in seawater.

Location	$C_{fi} = \left(\frac{C_{Ai}}{C_{Ni}} \right) - 1$		
	Cd	K	Na
Reference	0	0	0
Standard	-0.4	30.75	306.9
Aint	16.6	42.65	317.1
A1	38.6	40.4	109.7
A3	18.8	53.45	297.7
A5	38.6	58.85	318.8
B1	5.6	40.4	312.4
B3	12.2	40.1	319.3
C1	12.2	36.95	316.9
C4	45.6	44.45	347.3
C5	-0.6	-0.9	0.8
D1	21	33.65	296
E GOLF	192.6	34.7	311.3
F2	43	37.55	312.7
F4	36.8	41.3	309.5
H0	220.6	36.05	312.2
T S P	120	37.1	327.4

It is clear to us from Table 4, in which the extent of pollution of sea water with metals and heavy metals is determined, where we note that for cadmium metal, the ideal value of pollution, which should be less than 2.5, was in reference, standard and C5 samples, while we note that

most of the other samples exceeded the unlimited degree. It is not allowed and, E Gulf, H0 and TSP has reached the critical degree of pollution.

Table 4: Shown the value of different degrees of water pollution with heavy metals (Cd).

Location	Cd			
	Ideal, Less 2.5	Safe, (2.5-5)	Risky, (5-50)	Polluted, Up 50
Refe	0			
Stan	-0.4			
Aint			16.6	
A1			38.6	
A3			18.8	
A5			38.6	
B1			5.6	
B3			12.2	
C1			12.2	
C4			45.6	
C5	-0.6			
D1			21	
EGOLF				192.6
F2			43	
F4			36.8	
H0				220.6
T S P				120

we note that most of the other samples exceeded the degree of luminescence It is not allowed and the sample, A3 and A5 has reached the critical degree of pollution.

It is also clear to us that lead metal was the potassium pollution value, which should be less than 2.5, was in the same samples of where we note that for element of potassium, while we notice most of the other samples exceeded the degree of contamination that is not allowed and reached the critical degree of pollution Most of the samples have a dangerous degree of contamination except in the reference sample and sample C5 was at the ideal allowable pollution value.

Table 5: Shown the value of different degrees of water pollution with heavy metals (K).

Location	K			
	Ideal, Less 2.5	Safe, (2.5-5)	Risky, (5-50)	Polluted, Up 50
Refe	0			
Stan			30.75	
Aint			42.65	
A1			40.4	
A3				53.45
A5				58.85
B1			40.4	
B3			40.1	
C1			36.95	
C4			44.45	
C5	-0.9			
D1			33.65	
E-GOLF			34.7	
F2			37.55	
F4			41.3	
H0			36.05	
T S P			37.1	

It is clear to us from Table 6, that sodium metal was the ideal pollution value, which should be less than 2.5, was in the same samples of where we note that for element of sodium, while we notice most of the other samples exceeded the degree of contamination that is not allowed and reached the critical degree of pollution Most of the samples have a dangerous degree of contamination except in the reference sample and sample C5 was at the ideal allowable pollution value.

Table 6: Shown the value of different degrees of water pollution with heavy metals (Na).

Location	Na			
	Ideal, Less 2.5	Safe, (2.5-5)	Risky, (5-50)	Polluted, Up 50
Refe	0			
Stan				306.9
Aint				317.05
A1				109.7
A3				297.65
A5				318.8
B1				312.35
B3				319.25
C1				316.85
C4				347.3
C5	0.8			
D1				296
E-GOLF				311.3
F2				312.65
F4				309.5
H0				312.2
T S P				327.35

Table 7: seawater quality classification based on adopted and modified pollution indices classes.

Index method used	Class source	Classes	Degree of Pollution	No. of samples	% of samples in each class
Contamination degree	Cd	Less 2.5	Ideal	3	26.475%
		(2.5-5)	Safe	0	0%
		(5-50)	Risky	11	47.05%
		Up 50	Polluted	3	26.475%
Contamination degree	K	Less 2.5	Ideal	2	17.65%
		(2.5-5)	Safe	0	0
		(5-50)	Risky	0	0
		Up 50	Polluted	15	82.35%
Contamination degree	Na	Less 2.5	Ideal	2	17.65%
		(2.5-5)	Safe	0	0
		(5-50)	Risky	0	0
		Up 50	Polluted	15	82.35%

4. Conclusion

Tobruk harbor is one of the most polluted areas due to the adverse effect of effluents from land-based sources. Domestic untreated wastewater and fishing activities may be the major sources of observed higher levels of heavy metals contamination. The Tobruk water desalination plant is considered one of the most important vital sources on which most of the residents of Tobruk depend for drinking water, so increasing the percentage of heavy metals beyond the permissible limits may expose the plant to several problems, including the disruption of the work of some equipment as well as may have an impact in terms of health.

The Gulf of Tobruk and the surrounding area suffer from sewage discharge, oil discharges, and changing motor oils, which caused pollution with these heavy metals.

The concentration averages of the investigated metals in seawater were ranged in the order of cadmium, Potassium and sodium (0.22- 1.108), (0.002 - 1.197) and (0.02 - 6.966) respectively, Which makes the sea water has entered the dangerous stage, Which leads us to work on a special protocol to reduce seawater pollution in order to preserve marine life and the only source of drinking water for the city.

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