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Determination of Heavy Metals Pollution in Tobruk Bay

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Abstract: The aim of the study was to assess the degree of pollution of the Bay waters by heavy Metals and the extent of the impact of this pollution on drinking water in the city. This study included measuring the concentration of heavy metals Cr, Zn, Ni, Cu, Pb, Co, Cdin the Gulf waters where five points were selected, namely Municipal drain pipe, suction of water for desalination plant, Hariga Terminal for loading of oil for export, San George resort, Commercial port. Samples were collected and tests were conducted during the four seasons. These tests were performed using the plasma / atomic emission atomic induction spectrometer (ICP / AES). The concentrations of heavy metals were high in the Bay waters and therefore increased in drinking water resulting from the desalination of Bay water. When comparing the concentration of heavy Metals of drinking water with WHO specifications, as well as Libyan specifications, they were found to have exceeded the limit. The results obtained show that there is a large pollution of the Bay water by heavy Metals and this is considered to have a negative impact on the quality of drinking water as well as on the deterioration of the marine ecosystem in addition to the health impact on the practitioners of marine sports activities.

Keywords: Tobruk Bay, Marine Pollution, Heavy Metals, Pollution Indicators

1. Introduction

The pollution of the marine environment with heavy metals has become one of the most important global problems at present. They are indestructible and most of those Metals have Toxic effects on living organisms [1]. Heavy metal pollution is a particular concern, given the Potential toxic impact and bioaccumulation potential in aquatic ecosystems [2, 3]. Heavy metals found in the marine environment come from natural sources and human sources.

Natural sources are often present at low concentrations but anthropogenic sources have higher concentrations, causing environmental problems [4, 5]. The natural sources of heavy metals are soil erosion, rock temperament, and the dissolution of water soluble salts, While human resources are discharged directly from industrial and domestic wastewater to aquatic ecosystems [6, 7]. Heavy metal enters the marine environment and is dispersed throughout the water and then deposited in the sediment. The concentrations of heavy metals in sediments used for detection source and history of pollution [8]. Sea water in Tobruk Bay is at risk of many contaminants, such as domestic wastewater, industrial wastewater, shipping, potential accidents, port services and sewage services [9, 10]. Water discharge wells and water balance vessels in Tobruk Bay as well as water related to port services. There are many commercial and other ports for exporting oil and on the southern side of Tobruk oil refinery, which is a source of oil pollution in the Bay of Tobruk. There is also a desalination plant where the Bay water is used to produce drinking water which has the role of pollution by discharging the water of the back line of the evaporators. This water is very saline, high temperature and polluted with chemicals used in chemical treatment. This desalination plant is the main source of drinking water in and around Tobruk city to provide drinking water to the population of 200,000

people. These pollutants contributed to the pollution of the beaches of Tobruk Bay, making people refrain from using these beaches;this is in addition to concerns about contamination of drinking water from the desalination plant by heavy Metals. The presence of heavy metals in the Bay waters and their concentrations will be studied, with a test to determine the presence of heavy Metals in the drinking water produced by the desalination plant.

2. Materials and Methods

2.1. Area of the Study

The area selected for this study is the Tobruk Bay. TheTobruk city is located in the eastern part of Libya which is about 150 kilometers away from the Egyptian border. Tobruk Bay is located east of the city between the following coordinates:

At the end of the Gulf:
E235758.58 N320437.63
Starting of the Gulf
E240049.51 N320531.56

The length of the Gulf is about 5 km and its width at the entrance of the Gulf is 2 km and at the end is 0.6 km. The depths are between 5 to 16 meters in different parts of the Gulf.

2.2. Sampling and Analytical Methods

The following five sampling locations have been selected for this study in Tobruk bay:

Location 1: Municipal drain pipe
(Latitude: N 32°07′65″; Longitude: E 23°96′98″)
Location 2: The location in the bay where is suction of water for power station
(Latitude: N 32°06′42″; Longitude: E 23°98′45″)
Location 3:Hariga Terminal for loading of oil for export.
(Latitude: N 32°06′37″; Longitude: E 23°99′38″)
Location 4:San George resort
(Latitude: N 32°06′89″; Longitude: E 24°00′53″)
Location 5: Commercial port
(Latitude: N 32°07′63″; Longitude: E 23°97′54″)

Samples were collected from five sites distributed in the Bay as described and shown in the map (Figure 1). The water samples were collected from water surface by 50 cm. As for the sample of drinking water was taken from the main reservoir through which the distribution of drinking water to the city of Tobruk. The concentration of heavy Metals of drinking water will be measured to ensure the quality of drinking water.

Figure 1. *Seawater Sampling Locations in Tobruk Bay.*

The water samples were collected in 500 ml high density polyethylene bottles which were cleaned by acid, rinsed with distilled water and dried. The seasonal water samples were collected at the beginning of autumn 2016 until the summer of 2017. Bay water samples and drinking water were collected in polythene bottles after washing several times with 10% diluted nitric acid and then washed with salt-free water. All samples were filtered through 0.45 µm filter paper and then Seawater and drinking water samples were acidified by adding 10 ml from high purity nitric acid. The determination of the traces of metals is carried out by Inductively Coupled Plasma/ Atomic Emission Spectroscopy ICP/AES. [11] Standard operating conditions of the instrument were set during the analysis for heavy metal Metals including cobalt, nickel, copper, zinc, cadmium, lead and chromium in seawater. All results obtained were concentrated in mg/L.

3. Result and Discussion

3.1. Heavy Metals in Seawater

The concentration of heavy Metals for five samples from different locations in Tobruk Bay was measured in spring, summer, autumn and winter and the results were as shown in Table 1. In the study and analysis of the results, it was found that there are very high concentrations of some heavy metals where the concentration of nickel ranges between 5.3 to 281 mg/L, the zinc concentration ranges from 13 to 405 mg/L,

andthe lead concentration ranges from 1.8 to 51mg/L. In addition to the concentration of chromium, which ranges from 15 to 4260mg/L, it is worth mentioning that the highest concentrations of most of the heavy Metals were in the spring. As for the rest of the Metals there was a high concentration but less than the previous heavy Metals. Where the concentration of a Co element was from 0.0 to 6.3mg/L. a Cu element with a concentration from 8 to 110 mg/L, and a Cd between 0.0 and 2 mg/L. Heavy metal concentrations in the waters of the Tobruk Bay have been found in the following Sequence:

Cr > Zn> Ni >Cu > Pb>Co>Cd

The maximum values ofNi, Zn, and Cuwere found at sample No. 2 (spring) and maximum value of Pb and Cd was found at sample No 1.(spring).

Table 1. *Concentrate heavy Metals for samples.*

Sampling locations		HEAVY METAL CONCENTRATION (mg/L)						
		Co	Ni	Cu	Zn	Cd	Pb	Cr
Spring	1	1.7	48	52	54	2	94	489
	2	1.38	281	110	405	1	37	4260
	3	6.3	161	53	151	0.3	13.5	1849
	4	3	117	34	129	0.4	12.5	1358
	5	2.56	41	11	57	0.02	5.2	461
Summer	1	0.8	0.87	25	17.6	0.0	51.6	85
	2	0.01	9.22	15	16.23	0.0	19	39
	3	0.0	5.2	15	20.4	0.07	32.3	28.4
	4	0.02	5.7	18	14	1.2	35.5	44
	5	0.7	5.3	12.12	13	0.1	13.6	44.5
Autumn	1	0.6	9.6	20	21.5	0.5	30	110
	2	0.01	10.5	11.5	20	0.1	12	95
	3	0.02	9	9	24	0.05	16	40
	4	0.02	13	15	31.5	.2	20	450
	5	0.5	16	14	33.2	0.1	10	140
Winter	1	0.07	11.8	8	29	0.13	1.8	159
	2	0.22	16	11.2	39	0.12	8.37	167
	3	0.1	6	8	20	0.1	20	15
	4	0.28	14.5	14.5	43	0.22	8.6	246
	5	0.42	20	14.4	42	0.13	8.25	156
Blank sample		0.05	0.07	0.1	0.5	0.01	0.2	0.04

3.1.1. Cobalt (Co)

Cobalt enters the aquatic environment from sources, both natural and human and the natural sources from volcanic emissions. The human releases of cobalt in the aquatic environment are very limited and include: mining and processing of cobalt, production of alloys and chemicals, sewage, urban water runoff, and agricultural water runoff [12]. The results showed that the highest concentration of cobalt was 6.3 mg/L in the third sample of the spring season. The lowest concentration obtained was zero in the third sample of the summer season as shown in Figure 2.

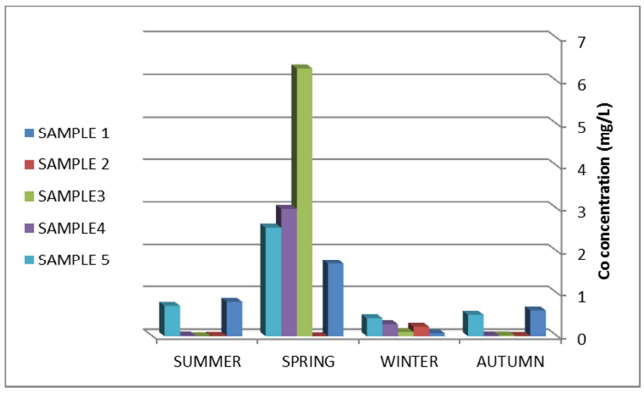

Figure 2. *Cobalt concentrations (mg/L) in Tobruk Bay.*

3.1.2. Nickel (Ni)

Nickel compounds are used as catalysts, dyes and batteries, where nickel comes from various industrial practices and from other sources to sewage. Thus dissolved nickel enters the marine environment through urban runoff, industrial effluents, and municipal discharges. In the second sample for the spring season, the highest concentration of nickel was found to be 281 mg/L and the lowest value was 0.01 mg/Las shown in Figure 3.

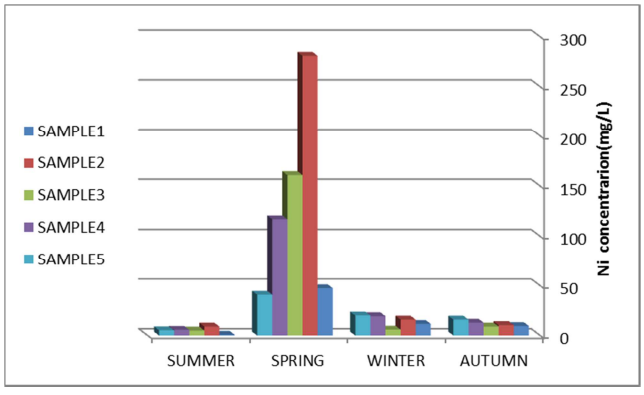

Figure 3. *Nickel concentrations (mg/L) in Tobruk Bay.*

3.1.3. Copper (Cu)

Copper is a vital element for the growth of most aquatic organisms. Although it becomes toxic to aquatic organisms at

low levels, copper input in natural water comes from a variety of sources including mining, smelting, domestic and industrial water. Electric steam production, as well as sewage water [13].

The highest concentration of copper was found in the second sample for the spring season, where the value was 110 mg/L, as shown in Figure 4.

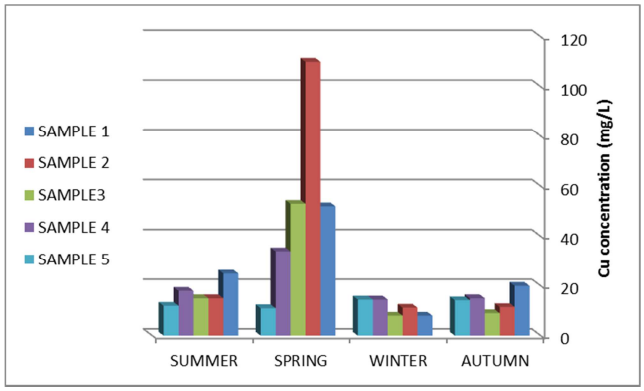

Figure 4. *Coppar concentrations (mg/L) in Tobruk Bay.*

3.1.4. Zinc (Zn)

High concentration of zinc Gulf water where the highest value of 405 mg/L in the sample No. 2 in the spring season and the minimum value was 13 mg/L sample No 5 in the summer season as shown in Figure 5. The source of this element is the local wastewater, municipal waste and paint and power plants.

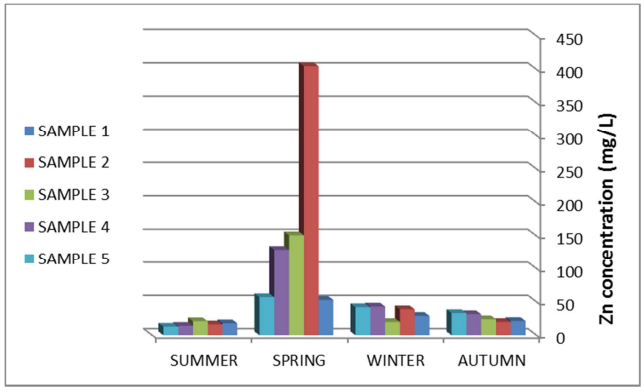

Figure 5. *Zinc concentrations (mg/L) in Tobruk Bay.*

3.1.5. Cadmium (Cd)

The presence of cadmium in the marine environment may be the cause of geology of soil catchments and runoff of phosphate fertilizers. Agricultural soil and disposal of nickel-cadmium-based batteries and cadmium-coated material. Cadmium is considered Highly toxic to freshwater and marine organisms. It accumulates biologically Through the food chain [14] As well as the waste of human activities and the disposal of municipal liquid waste. The highest cadmium concentration was 2 mg/L and the minimum concentration was zero at the same site with a different season as shown in Figure 6.

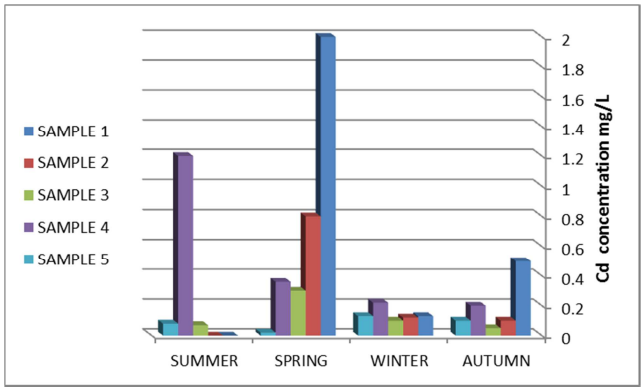

Figure 6. *Cadmium concentrations (mg/L) in Tobruk Bay.*

3.1.6. Lead (Pb)

The level of lead in the coastal environment is affected by human activities Such as automobile exhaust, domestic sewage Agricultural runoff, operation of the power station, and filtration of the protective paints used by fishermen Boats and fuels that contain diesel and gasoline [15]. This leads to a high concentration of lead levels in Bay waters The results showed that the highest concentration of lead was 94 mg/Lin the first sample of the spring season, the lowest concentration was 1.8 mg/Lin the first sample of the winter season as shown in Figure 7.

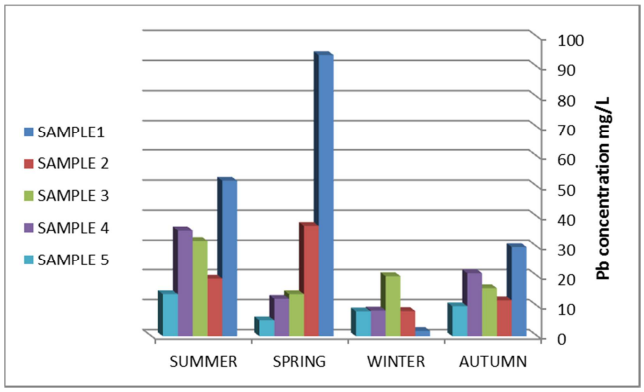

Figure 7. *Lead concentrations (mg/L) in Tobruk Bay.*

3.1.7. Chromium (Cr)

Chromium often accumulates in aquatic life, which increases the risk of eating fish that may be Exposed to high levels of chromium. Chromium enters the marine environment through liquid waste from chemical plants, paints and sewage. The concentration of the chromium element is higher for other Metals in the Bay water and the highest value reached 4260mg/L in the second sample of spring, and the lowest value was 15mg/Lin the winter season, as shown in Figure 8.

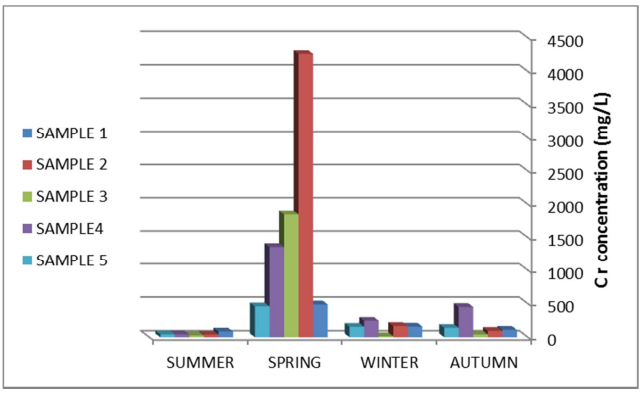

Figure 8. *Chromium concentrations (mg/L) in Tobruk Bay.*

3.2. Heavy Metals in Drinking Water

By studying the concentration of heavy Metals in the waters of Tobruk Bay and the results obtained, it was found that there was a high concentration of these Metals. Since the use of Bay water in the production of drinking water, which feeds the city of Tobruk was studied the contamination of drinking water with heavy Metals. The average number of drinking water samples was taken from the main reservoir through which drinking water was distributed to Tobruk, The concentration of the heavy Metals was measured and the results were as shown in the table 2.

Table 2. *The concentrations of Heavy metals in drinking water.*

Samples	HEAVY METAL CONCENTRATION (mg/L)						
	Co	Ni	Cu	Zn	Cd	Pb	Cr
DWS	1.09	8.02	12.4	27.05	0.16	18.9	83.7
WHO	0.0	0.02	1.0	5	0.005	00.1	0.05
LNCSM		0.02	1.0	3	0.003	0.005	0.05

DWE: Drinking water sample.
WHO: World Health Organization.
LNCSM: Libyan center for standardization and metrology.

It was found that the concentration of heavy Metals in drinking water for the city of Tobruk was much higher than the permissible values, which were determined by the World Health Organization and the Libyan specifications for drinking water. A study of these results showed that drinking water is contaminated with heavy Metals due to contamination of the waters of Tobruk Bay, which is considered the feedstock of the drinking water production plant. The high concentration of heavy Metals in drinking water is higher than the permissible limit, causing health problems in people who use this water. We illustrate some of the health effects of heavy metal contamination in these people as shown in the table 3.

Table 3. *The health effects of heavy metals.*

Metals	Health effects
Co	The lack of standards for drinking water reflects the minimal risk
Ni	Lung cancer, throat, stomach, nose and sinus, Systemic toxicity
Cu	Anemia, digestive disturbances, liver and kidney damage Gastrointestinal irritations
ZN	dehydration, abdominal pain nausea and dizziness
Cd	Highly toxic; causes disease-painful rheumatic cardio vascular system affected; gastro intestinal upsets and hyper tension.
Pb	Reduces mental capacity, hearing loss, hypertension, death at high levels
Cr	Skin irritation, lung tumors gastrointestinal effects, damage to the nervous system and circulatory system, accumulates in the spleen, bones, kidney and liver

4. Conclusion

The results obtained after measuring the concentration of heavy metals in Tobruk showed that there was a significant increase in the concentration of these Metals, where the concentration of Cr to 4260mg/L, Pb to 94mg/L, Zn to 405 mg/L, copper to 110 mg/L, Ni to 281mg/Land cobalt to 6.3 mg/L. This has caused pollution of drinking water because the place where the seawater is drawn to the desalination plant is located in this polluted Bay. The pollution of the Bay of Tobruk is due to several sources, the most important of which are the sewage water entering the Gulf waters without treatment, as well as the leakage of oil during the export of oil from the port of oil, as well as the water balance of ships being disposed of inside the Gulf as well as other activities such as ship painting and maintenance. All these pollutants may lead to deterioration of the quality of the Bay waters and the degradation of the marine ecosystem. In addition to its negative impact on the health of people who practice some marine sports activities. The absence of treatment and the long-term exposure to these discharges will lead to dangerous levels of heavy metals which maybe lead to destruction of marine life and may affect people living near the port.

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