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Investigating Study on the Total Hydrocarbons Pollution in the Waters of the Shores at Zawiyah Beaches, Libya

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ABSTRACT

Pollution of the marine environment as a result of various human activities can harm marine life, which naturally leads to impeding marine environment projects. This study aimed to estimate the total concentrations of hydrocarbons, which threaten marine wealth, in the waters of the shores of the Zawiyah region during the months of December 2017 and June 2108, the method of wet digestion using concentrated hydrochloric acid was used, and then the total hydrocarbons were estimated by the gravimetric method. The results of the total hydrocarbon concentrations in the beach water samples of the studied area were generally low, with a marked increase in these concentrations in the western shore waters of the area near the Zawiyah refinery and the Harsha power station, where 21.47 µg /l was the highest average concentration recorded in this study, while 5.37 µg /l was the lowest average concentration recorded. The obtained results

from this study can be quite consistent with the results of the study conducted by the United Nations Environmental Protection Program (UNEP) in the coasts of several regions of the world, among of which Libyan coast, where the average concentration of total hydrocarbons along the Libyan coast was 13.40 µg /l.

Keywords: Pollution, Marine-environment, Hydrocarbon, Libyan-Coast.

1. Introduction

Pollution of the marine environment is the introduction of materials or energies into the marine environment, either directly or indirectly, and with a concentration that could harm human health, marine life, and the marine environment in general. This pollution leads to an increase in the concentration of some compounds in the marine environment. In the Mediterranean Sea, pollution is related to the increased industrialization of the surrounding countries [1]. A very common practice in Libyan coast is the open dumping of industrial effluents into the sea as well as the sewage water. Hydrocarbons, one of the most significant pollutants, can persist for years [2], with dangerous effects on coastal environments, and can also have negative effects on both the ecosystem and the marine biodiversity [3].

Hydrocarbon chemicals are major components of crude oil and are classified as polycyclic aromatic hydrocarbons, aliphatic saturated hydrocarbons, aliphatic unsaturated hydrocarbons, and alicyclic

saturated hydrocarbons [4]. The impact of these four categories on the ecosystem is especially concerning because of their specific toxicity [5]. Sources of petroleum hydrocarbons in the marine environment are both natural and unnatural and may come from natural oil seeps and oil spill. Unnatural (industrials) sources are included refineries, storage facilities, municipal, industrial wastes and transportation activities. In addition to that, in the last several decades, several oil spill accidents have happened all over the world, and enormous amounts of crude oil have been released into the aquatic environment [6].

Inputs from natural sources are usually low compared to those from industrial sources, and thus the inflow of municipal effluents, stormwaters and industrial discharges into the sea are considered to be the main source of hydrocarbons pollution. [7] Such discharges are mainly from the coastal urban areas and although at low concentrations may not pose any immediate threat, but could trigger a great challenge over a long period of time [8], and its impacts on aquaculture could be very severe because oil has a tendency to bio-accumulate in the tissues of fish, molluscs, mussels and other mammals [9, 10].

Studies [11] have shown that the amount of oil that seeps into the oceans from ships and tankers is estimated at (1%) of the transported quantity, given that each ton of spilled oil can be distributed over an area (10-12 km^2). In a previous study conducted by the United Nations Environmental Protection Program (UNEP) for the coasts of several

regions of the world, the average concentrations of hydrocarbons were recorded to be in between 580 (µg\l) for French Coast and 3.26 (µg\l) for Italian Coast, while the in Libyan Coast the concentrations was 13.40 (µg\l) [12]. In an international symposium on combating pollution and protecting marine wealth in the Mediterranean, Al-Ezabi [13] indicated to a study conducted along the Libyan coast to find out hydrocarbons concentrations, the results were recorded in the Table (1).

Table (1): Average concentrations of hydrocarbons on the shores of Libyan coastal cities, in units (µg\l) [13].

Region	**1980**	**1984**	**1987**
Zwara	16.65	3.55	3.50
Zawiyah	2.68	10.35	6.95
Tripoli	4.15	11.63	4.55
Sidra	4.34	7.05	-
Benghazi	2.91	3.70	-

Furthermore, other studies such as Gerges and Durgham studies [14], have shown relatively high level of pollution by petroleum products in some areas north and south of Brega Marina, where the concentration of total hydrocarbons in sea water reached 17.2 µg / l, and this high level of pollution is attributed to the direction and speed of the wind, while the same study showed low concentrations for hydrocarbons 4.8 µg / l in the waters of Benghazi beach.

For a long time, Libya showed little interest in hydrocarbon pollution and particularly that in open seawater. To our knowledge, no studies have addressed the hydrocarbon levels along the Zawiyah region,

more specifically in the water coast and for the lack of references and research in this area related to the shores of the Zawiyah region. Therefore the first objective of the current study was to estimating the total hydrocarbon concentrations in the waters of the sea shores in the Zawiyah region and comparing them with the permissible range locally and internationally. This will contribute to the preparation of a database that gives the total hydrocarbon concentrations in seawater in the Zawiyah region. The second objective of this paper is to address the importance of understanding the effect of the total hydrocarbon on the marine environment and draw recommendations regarding total hydrocarbon concentrations in the coastal waters of the region and the extent of their impact on the safety of the marine environment and marine life.

2. Materials and Methods

2.1 Sample collection

The samples are collected from the Zawiyah coastal marine area which is located on the Mediterranean Sea, in the western coast of Libya. Sixteen samples of sea water were collected from the surface water in shores of the Zawiyah region according to the standard methods [15] during December 2017, and June 2018 eight samples each time. The samples are taken in winter and summer times from the same areas for comparison, and because of the fact that oil spills from land based sources and transportation activities are reportedly

more damaging in cold climates than in the warmer climates [16]. The study area was conducted from Mothred in the west to Jaddaim in the east. The location of the samples are shown in Figure 1.

Figure (1): Map of the collected Samples for the investigated Zawiyah coastal marine area at 32.763° latitude and 12.737° to 12.721° range of longitude, with a distance between samples ranging from 2 km to 4 km.

Sample number, cods, name of the sampling site, and the size used are shown in Table 2.

Table (2): Sample number, name of the sampling site, and the size used for the analysis and sample cod.

Sample number	The name of the area from which the sample was taken	The volume used in ml for total hydrocarbons	December 2017 Sample Cod	June 2018 Sample Cod
1	One km west of the Mothred Beach	1000	101	201
2	One km east of the Mothred Beach	1000	102	202
3	One km west of the power station in Harcha	1000	103	203
4	In-between the west of Al-Zawia refinery and the power station in Harcha	1000	104	204
5	One km east of Al-Zawia Refinery	1000	105	205
6	Espan Beach	1000	106	206
7	Dila Marina	1000	107	207
8	Jaddaim Beach	1000	108	208

2.2 Sample preparation

During preparing the samples, all used tools and glassware were thoroughly washed with distilled water twice and then submerged in a mixture of concentrated nitric acid and hydrochloric acid at a ratio of (2: 1). Then they washed again and several times with distilled water. The samples were prepared by taking a volume of 1000 ml of sea water and placed in standard flasks with a capacity of 1000 ml sealed, and 1 ml of concentrated hydrochloric acid was added to it, and the

samples were kept directly in the beakers at room temperature until the samples were submitted for analysis [12].

2.3 Samples analysis

1. One liter of the sample on which the required preservation was performed was placed in a separating funnel of 1000 ml capacity and 5 ml of dilute hydrochloricacid (1: 1) was added to it.
2. The sample vial was first washed with 20 ml of solvent (hexane) and added to the sample and then washed again with 20 ml of solvent and added over the sample in a separation funnel as well.
3. Shake the solution well for two minutes, then leave for ten minutes to settle and separate the aqueous and organic layers.
4. The aqueous layer was taken to a holding flask and the organic layer was left to filter over a filter paper containing (0.5-1.5) gram of sodium sulfate (it absorbs water molecules that may be present in the organic layer) placed on a funnel above a small beaker of known weight.
5. The process of washing the aqueous layer with solvent was repeated twice. The organic layer was left on the filter paper to collect both in the beaker and the filter paper was washed with (10-30) milliliters of solvent.
6. Heat the beaker over a hot plate or in an oven-drying to dryness.
7. The beaker was weighed after being cooled to find the weight of the remaining materials.

8. The total hydrocarbon concentrations in the water samples were calculated using the following equation [15]:

$$C = \left[\frac{(A - B) \times 1000}{V} \right] \times 1000$$

Where :

C = Concentration of the unknown sample in μg / L.

A = Weight of the beaker and materials remaining on it (in milligrams).

B = Empty beaker weight (in milligrams).

V = Sample volume (in milliliters).

The validity of the obtained results is evaluating statistical by repeating the concentration measurements three times and then the average readings were calculated (Mean), its standard deviation (SD), and the relative standard deviation (RSD).

3. Results and Discussion

The results of this study are shown in Figure (2) and Figure (3). Figure (2) shows the average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of December 2017. From the figure one can see that the samples 103, 104 and 105 show largest values these large values might be attributed to the fact that theses samples were collected from areas that situated near two large industrial plants (Al-Zawia refinery plant and Harsh power plant).

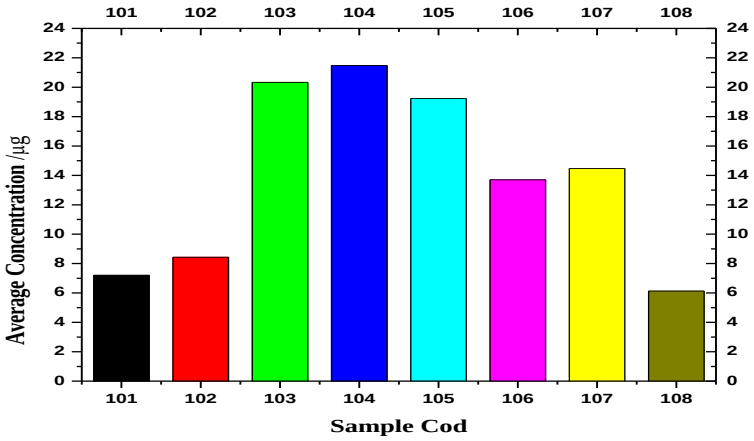

Figure (2): Average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of December 2017.

On the other hand the low value of the average concentration of total hydrocarbons were shown in samples 101, 102 and 108. The low concentration values in these samples indicates less pollution in these areas comparing with the other five regions that investigated in this work. This results indicates that rates of pollution with this type of pollutants are still in their infancy when comparing the results of the current study with the results of other studies [12, 17]. This means that the concentrations of hydrocarbons in the Zawiyah coasts is considered low concentrations when it compared to the local and global the recorded levels.

Figure (3) shows the average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of

June 2108. Despite of the time at which the sample was taken, once again the samples 203, 204 and 205 showed the largest values and the samples 201, 202 and 208 showed the lowest values of the average concentration of total hydrocarbons.

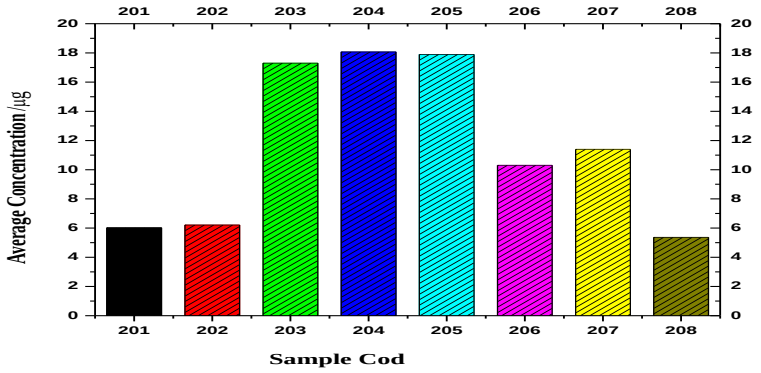

Figure (3): Average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of June 2108.

However, from the results three important notes should be point out; first note is the concentrations in the eastern coasts of the study region during both December and June appeared to have higher total hydrocarbon concentrations than the western coasts, The second note is the concentrations during December were almost higher than the concentrations during June, and third note is there were small changes in the actual value of the average concentration of total hydrocarbons as shown more clearly in table (3) and table (4). All the previous notes are attributed to the variation in the rate of evaporation during the

winter and summer season, in addition to the nature of the geographical area and marine currents, which can transport these pollution materials to great distances from the places of their leakage and access to the sea water, and the tidal process has a great effect in dispersing hydrocarbons to static and protected areas, that is, in which the movement of waves such as lakes is less in gulfs and ports, which led to the increase in total hydrocarbon concentrations in them to high levels.

The results of the statistical analysis namely standard deviation (SD), and the relative standard deviation (RSD) are shown in the table (3) and table (4), clearly from the results that the discrepancy was clearer in the month of December as well as June.

Table (3): Average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of December 2017.

Sample Cod	Average Concentration (µg\l)	Standard Deviation (SD)	Relative Standard Deviation (%RSD)
101	7.20	0.52	7.2
102	8.43	0.87	10.3
103	20.33	2.92	14.4
104	21.47	0.87	4.0
105	19.23	0.75	3.9
106	13.70	0.42	3.0
107	14.47	0.46	3.2
108	6.13	0.33	5.4

Table (4): Average concentration of total hydrocarbons in the sea water in the coasts of the Zawiyah region during the months of June 2018.

Sample Cod	Average Concentration (µg\l)	Standard Deviation (SD)	Relative Standard Deviation (%RSD)
201	6.02	0.37	6.1
202	6.21	0.21	3.4
203	17.30	1.95	11.3
204	18.07	1.81	10.0
205	17.90	1.27	7.1
206	10.30	0.71	6.9
207	11.40	0.51	4.5
208	5.37	0.26	4.8

This discrepancy may be due to the nature of the coastal geomorphology (coastal topography) and to the difference in sea currents and their directions during the winter and summer seasons, and the phenomenon of tides has a major role in the accumulation of hydrocarbons in areas such as lakes and bays (onshore) without other areas (deep waters). Another reason that led to this variation is also the total dissolution rate of hydrocarbons in the water in addition to the biological oxidation processes, which may differ according to the conditions of the region according to the activities of oil-breaking bacteria [18].

The results of this study are consistent with the results of the study that conducted by the United Nations Environmental Protection Program (UNEP) [12] in the coasts of several regions of the world

where the average concentration of total hydrocarbons along the Libyan coast in 1977 was 13.40 (µg\l), and with the passage more than 40 years on that study and as a result of the increase in navigation traffic, industrial development and an increase in the demand for oil and the frequent accidents of ships and oil tankers, all this led to an increase in the total concentrations of hydrocarbons in all regions of the world, including the coasts of Libya. Furthermore the obtained results are in a good agreement with the results of the study conducted by Garges and Durgham [14], carried out in North and South Marsa Brega, in which the concentration of hydrocarbons was 27.2 (µg\l), which quite close to the results of the current study, and this could be due to the similarity between the two regions of study in terms of industrial activities that exist there. As there is a port for the export of oil in Brega, that similar to the port for the export of oil in Zawiyah region ,which may lead to this remarkable rise in the concentration of hydrocarbons in the port and its surrounding areas.

4. Conclusions

This study was conducted to find out the extent to which the shores of the Zawiyah area are polluted with total hydrocarbons, and to draw attention and alert to the danger of these chemical pollutants and the extent of their impact on marine organisms and fish wealth in order to preserve public health and the environment. In this research, a comprehensive survey was made on the coast of the Zawiyah region,

with a distance of about 25 km to estimate the total hydrocarbon concentrations on the shores of the area. The total hydrocarbon concentrations in the marine waters of the study area were within the natural pollution rates compared to other local and international studies, and the concentrations in the eastern coasts of this region during both December and June were almost higher than the western coasts. However, the concentrations during December were almost higher than the concentrations during June. This variation in results is due to the rate of evaporation during the summer season, in addition to the nature of the geographical area and marine currents, and the tidal process has a great effect in dispersing hydrocarbons to static and protected areas, which led to increase the total hydrocarbon concentrations in them to high levels.

5. Recommendations

Through this study and the results reached, three important recommendations must be stated:

1. The establishment of power plants, oil refineries, and any other industries resulting in pollution with total hydrocarbons should be far from the shores of cities and residential areas.

2. Establishing a periodic monitoring program for pollutants in general in factories, ships and oil loading and unloading platforms.

3. Providing information on the characteristics and specifications of liquid wastes and taking into account the scientific conditions and principles that take into account environmental risks.

6. References

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