Comparative study of hydrocarbon pollution before and after rainfall in Al-Gharraf River in Thi-Qar province – Iraq

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Abstract. The difference between the seasons of the year and the fall of rain has a significant impact on the degree of pollution of hydrocarbons in the water of rivers in the area falling on them, to study the degree of hydrocarbon pollution in Al-Gharraf river in Thi-Qar province, the Samples were collected from water, sediments, Phragmites australis and Ceratophyllin demersum from this river that passing through Al-Fajr, Qal'at Sukkar and Al-Rifa'I cities in October 2018 and January 2019. The results showed that the concentration of TPH were increasing in January (after rainfall); as well as according to the order of the areas mention above the amount of increase in TPH In the water (17.7, 22.3, 18.9) μg / L , while in the sediments (647, 904, 626) μg / g D.W , however in Phragmites australis (2.00, 2.00, 3.19) μg / g D.W and Ceratophyllin demersum plant has reached an increase (1.88, 4.83, 5.2) μg / g D.W

Keywords: Total Petroleum hydrocarbons TPH , Al-Gharraf river, water pollution, oil deposits.
INTRODUCTION

Total petroleum hydrocarbon (TPH) is a term to describe a large family of hundred chemical compounds that originally is derived crude oil. Crude oil is used to production a lot petroleum products, That can cause pollution to the environment[1]. TPH is a mixture of chemicals, but they are made mainly from carbon and hydrogen, it is called hydrocarbons. Some chemicals that may be found in TPH are hexane, benzene, toluene, jet fuels, mineral oils, naphthalene and xylenes, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals[2]. The presence of TPH in river water is a dangerous and disturbing for the public. Many of these products or their metabolites to be toxic to living organisms, And affect the lives of organisms in the aquatic and terrestrial environment. It is inevitable that sizeable quantities of these products will find way into the water, soil, air and plants by mishandling, spilling or leaking of underground storage tanks and oil pipes[2]. Oil Leak devastate a soil and aquatic systems and cause alteration in important microbial process [3]. Biologically, they have Toxicity on aquatic life (Edema, 2008). There are many sources Which lead to pollution by TPH in our environment which include petroleum extraction, transportation, refining and consumption [4]. Water pollution is one of the greatest problems facing the environment as a result of the complex structure of pollutants that become more complex when exposed to weather conditions as well as their toxic effect And its relationship to human. There are many pollutants that bring to the water rivers, including sewage and waste collected in pipes or channels and put into the River water and these sources can be controlled and reduce the harmful effects by treatment before the access to river water. As well as waste from cities or agricultural land and It is considered From sources that are difficult to treat Most of them reach to rivers through Rainfall or melting of snow [5].

The solubility of oil in water is low [6] and depends on the chemical composition of crude oil and temperature [7]. Alkanes are less soluble in water than aromatic hydrocarbons [8]. The most volatile components of crude oil are aromatic compounds with low molecular weights such as benzene, toluene and Xylene [9]. This property is of great importance in estimating the fate of the oil spill as well as the amount of oil and bioremediation processes for oil pollution or spot oil [10].

Study Area

Selected three stations on Al-Gharraf River to complete the current study as in Fig (1). To determine the probability of contamination of the area by TPH, And the problem of pollution spread result of combustion operations was selected part of the Al-Gharraf river Which extends from Al-Fajr city through Qalat Sukkar city and up to Al-Rifai district Where this area is located near the Al-Gharraf oil field Where is located about 8 km north of the Al-Rifai district and this area has been divided into three section:

Station (1) : - North at the Al-Fajr city and Considered is a control station, which is far from the oil field area 23 km.
Station (2) : - At the Qalqat Sukkar city, which is adjacent to oil field.
Station (3) : - In the Al-Rifai district south of the Al-Gharraf oil field, which is 8 km from the oil field.
Fig (1):- Three stations on Al- Gharraf River

Collection of samples
Water samples from the three stations were collected by 5 liter glass bottles of dark brown color, surrounded by a heavy metal netting from the bottom by a piece of 15 kg lead. These vents have small openings (2-3 cm) for slow filling and slow diving. After the bottle is full, pull it to the top and close immediately by the payment. It was added 50 mm of CCl4 carbon tetrachloride and samples were collected at a depth of 1 m.

The sediment samples were collected by the Van veen grab sampler and then the samples were stored in aluminum foil and placed in a refrigerated box until they reached the laboratory. Samples Phragmites australis and Ceratophyllin demersum were collected by hand and brought to the laboratory.

Drying samples
Drain the sediment samples by using the Freeze Dryer, then the samples were grinded using a mechanical mill and then sifted with a sieve metal diameter 63 mm, then placed in glass containers to be ready for extraction. And cut Phragmites australis and Ceratophyllin demersum into small parts and then dried by drying device and the sample was grinded with an electric mill and sifted and then placed in clean glass bottles to be ready for extraction.

Methods of extraction:

- Extract hydrocarbons from water
  The method used by the United Nations Environment Program [11] has been used to extract hydrocarbons from water.

- Extract hydrocarbons from sediments
Adopted method [12] that followed by [13] In extracting hydrocarbons from sediments.

-Extracting hydrocarbons from Phragmites australis and Ceratophyllin demersum:
  Adopted method [14] In extracting hydrocarbons from Phragmites australis and Ceratophyllin demersum.

The result and Discussion

The concentration of TPH in water in the first station in October was the highest (41.2) μg/l and in October at the second station was the lowest concentration (33.1) μg/l (the second station is adjacent Gharraf oil field) while the third station, which is located south of the Gharraf oil field, higher than the second station in October and reached (37.4) μg/l as in table (1) and Figure (2).

Water is exposed to a lot of sources of pollution, including industrial designs resulting from various industries such as oil refineries and gas associated with oil extraction, paper industry, fertilizers, spinning, weaving, rubber and petrochemical industries [5].

In 2004, Aziz explained that the sources of TPH in the aquatic environment are due to the heavy sewage discharged into the river without treatment [15].

In January, there was a significant increase in TPH in water samples in all stations compared with October after the rainfall, that where highest concentration was recorded in the first station (58.9) μg/l, while in the second station, which is adjacent to the oil field It recorded the lowest concentration (55.4) μg/l and in the third station was higher than the second station (56.3) μg/l being located to the south of the oil field. As well as waste from cities or agricultural land and It is considered from sources that are difficult to treat Most of them reach to rivers through Rainfall or melting of snow (Talal, 2008)

TPH concentrations in sediments were in January 2019 (After rainfall) higher than the concentrations in October 2018 (Before rainfall) Concentrations in stations 1, 2 and 3 were in October, respectively (2292, 2113, 2374) μg/g D.W. But in January the concentrations in stations 1, 2 and 3 respectively (2939, 3017, 3000) μg/g D.W As in table (2) and figure (3).

The concentrations of TPH in January 2019 in the plants in our study (Phragmites australis and Ceratophyllin demersum) respectively, were higher than their concentrations in October 2018 before rainfall. It was in Phragmites australis in October (stations 1, 2 and 3) respectively (8.75, 9.20, 7.43) μg/g D.W, however in January after the rainfall in stations (1, 2 and 3) respectively (10.75, 11.20, 10.62) μg/g D.W. In Ceratophyllin demersum; the concentrations were in October in stations (1, 2 and 3) respectively (1.82, 0.92, 1.02) μg/g D.W while in January and after the rainfall in stations (1, 2 and 3) respectively (3.98, 5.75, 6.22) μg/g D.W. As we note Concentrations in Phragmites australis are higher than those in Ceratophyllin demersum. studied (Al-Khafaji, 2007) determination and concentration of total hydrocarbons in water, surface sediment and two distinct aquatic plants, Ph. australis and Typhadomingensis but Ph. Australis recorded higher concentrations from the other plants as in table (3, 4) and figure (4, 5).

When comparing the results in current study with the previous studies of Shatt al-Arab River and the Iraqi marine water, our study showed a significant increase in concentration TPH of water and sediment in Al-Gharraf river as in figure (5,6), this is
may be due to several factors including the establishment of new oil fields such as Al-Ahdab oil field located near this area in Wasit province which is located north of Thi-Qar province, which passes the river through it before entering the study area as well as Al-Gharaf oil field which is adjacent to the study area and negative effects associated activities of these oil fields as burning associated gas and increase industrial activity in this region as well as lower levels of water and increase the jetsam of waste water and domestic sewage and the lack to real treatments for this pollutants led to the rise of TPH in this part of the river.

**Recommendations**

1. Adopting the scientific method in the research and survey to identify the scientific facts.
2. Conduct a comprehensive survey of environmental problems and determine the causes and quality according to their location and try to develop solutions.
3. Treatment and improvement and development of water treatment plants before throw away to river.
4. Setting up monitoring stations to treat the waste of laboratories and factories before throw it to the environment.

Table (1) :- The concentration of TPH in water samples Before and during the rainfall season from Al-Gharraf river through period October 2018- January 2019 (μg / L)

| Stations | Concentrations in October 2018 (μg / L) | Concentrations in January 2019 (μg / L) | Amount of increase (μg / L) |
|----------|----------------------------------------|----------------------------------------|-----------------------------|
| 1        | 41.2                                   | 58.9                                   | 17.2                        |
| 2        | 33.1                                   | 55.4                                   | 22.3                        |
| 3        | 37.4                                   | 56.3                                   | 18.9                        |
Fig (2) :-The concentration of TPH in water samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg / L)

| Stations | Concentrations in October 2018 (μg / g) D.W | Concentrations in January 2019 (μg / g) D.W | Amount of increase (μg / g) D.W |
|----------|-------------------------------------------|-------------------------------------------|-----------------------------|
| 1        | 2292                                      | 2939                                      | 647                         |
| 2        | 2113                                      | 3017                                      | 904                         |
| 3        | 2374                                      | 3000                                      | 626                         |
Fig (3) :-The concentration of TPH in Sediment samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg /g) D.W

Table (3):- The concentration of TPH in Phragmites australis samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg /g) D.W

| Stations | Concentrations in October 2018 (μg /g) D.W | Concentrations in January 2019 (μg /g) D.W | Amount of increase (μg /g) D.W |
|----------|---------------------------------------------|---------------------------------------------|-------------------------------|
| 1        | 8.75                                        | 10.75                                       | 2.00                          |
| 2        | 9.20                                        | 11.20                                       | 2.00                          |
| 3        | 7.43                                        | 10.62                                       | 3.19                          |
Fig (4): - The concentration of TPH in Phragmites australis samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg /g) D.W

Table (4):- The concentration of TPH in Ceratophyllin demersum samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg /g) D.W

| Stations | Concentrations in October 2018 (μg /g) D.W | Concentrations in January 2019 (μg /g) D.W | Amount of increase (μg /g) D.W |
|----------|------------------------------------------|------------------------------------------|-------------------------------|
| 1        | 1.82                                     | 3.98                                     | 1.88                          |
| 2        | 0.92                                     | 5.75                                     | 4.83                          |
| 3        | 1.02                                     | 6.22                                     | 5.2                           |
Fig (5):- The concentration of TPH in Ceratophyllin demersum samples Before and during the rainfall season from Al- Gharraf river through period October 2018- January 2019 (μg /g) D.W

Table (5):- Compared to the concentrations of TPH in water from the Shatt al- Arab River and Al-Iraqi marine waters in previous times and the current study of Al- Gharraf river

| location                      | Time of study | Concentration (μg / L) | references |
|-------------------------------|---------------|------------------------|------------|
| Shatt Al Arab                 | 2000          | 2.5 – 47               | [16]       |
| The mouth of the Shatt Al Arab| 2000          | 31 – 80                | [16]       |
| Khor al-Zubayr                | 2002          | 4.6 – 22.6             | [16]       |
| Umm Qasr                      | 2002          | 2.34 – 2.52            | [16]       |
| North West Arabian Gulf       | 1993          | 2.6 – 3.7              | [17]       |
| Khour Abd Allah               | 2000          | 44 – 75                | [17]       |
| Iraqi Sea Water               | 2002          | 1.08 – 15              | [17]       |
| Iraqi territorial waters      | 2002          | 4.92 – 46.40           | [18]       |
| The current study             | 2018- 2019    | 37.4 - 56.3            |            |
Table (6):- Compared to the concentrations of TPH in sediment from the Shatt al-Arab River and Al-Iraqi marine waters in previous times and the current study of Al-Gharraf river

| Location                          | Time of study | Concentration (μg/g D.W) | References |
|-----------------------------------|---------------|--------------------------|------------|
| Shatt Al Arab                     | 1993          | 9.7 – 38                 | [17]       |
| The mouth of the Shatt Al Arab    | 1993          | 10.7 – 23                | [17]       |
| Khor al-Zubayr                    | 2002          | 21 – 178                 | [16]       |
| Umm Qasr                          | 2002          | 9.7                      | [16]       |
| North West Arabian Gulf           | 1997          | 2.4 – 5.8                | [17]       |
| Khor Abd Allah                    | 1991          | 1.4 – 1.7                | [19]       |
| Iraqi Sea Water                   | 2002          | 8.7 – 20                 | [16]       |
| Iraqi territorial waters          | 2002          | 16.34 – 192.34           | [18]       |
| The current study                 | 2018-2019     | 2113 – 3017              |            |

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