Total Petroleum Hydrocarbons and their relationship with Total Organic Carbon in the sediment from the Northern Part of Shatt Al-Arab River Basrah – Iraq

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Abstract

The current study deals with the concentrations of total petroleum hydrocarbons (TPH) and determination of the percentage of total organic carbon (TOC) and the texture components in the sediments of five stations selected in the northern part of Shatt Al-Arab River (Al-Qurna, Al-Sharish, Al-Shafi, Al-Deir and Al-Hartha) during the period from 2018 to 2019. The concentrations of TPH in the sediments were estimated using a fluorescence device. The lowest concentration was 7.933 µg/g dry weight at Al-Shafi station during the summer while the highest was 52.793 µg/g dry weight at Al-Deir station during the winter. The percentage of TOC content in the sediments ranged between 5.754% and 15.612%. It was noted that the texture of the sediments was of the silty clay type, and the average percentage of clay was 27.6%, silt (64.2%) and sand (8.2%). Statistical analysis showed positive correlations between both TPH and TOC in the sediments.

Keywords: Total Petroleum Hydrocarbon, Total Organic Carbon, Texture of sediments, Shatt Al-Arab River.

Introduction

Crude oil is a complex mixture of liquid and solid organic compounds (Akpor *et al.*, 2007). Hydrocarbons are organic chemical compounds composed mainly of carbon and hydrogen. These compounds represent the main component of oil, as they constitute 50%-98% of it (Zhu *et al.*, 2004). Hydrocarbons are poorly soluble in water and are easily adsorbed on the surfaces of suspended particles in the water column, after which they settle down, so that the sediments become a reservoir for many pollutants. The danger of these organic pollutants is their tendency to bioaccumulate in aquatic organisms (Ali *et al.*, 2015).

Most studies have indicated that hydrocarbons in water, sediments and biota come from two sources, the first of which is a biogenic source, as most aquatic organisms produce hydrocarbons or obtained them from their environment. These compounds

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reach the aquatic environment after the death of these organisms (e.g. phytoplankton, zooplankton, algae, crustaceans and bacteria) and the decomposition of their bodies (Al-Khatib, 2008). The second is an anthropogenic source, which results from oil and its derivative's transportation (Osuagwu *et al.*, 2013), industrial activities, accidents, spills, balance water, and washing of loading docks played an important role in polluting the aquatic environment with petroleum hydrocarbons (Anisuddin *et al.*, 2005; Al-Atbee, 2018). Also, gaseous emissions add large amounts of hydrocarbons through fuel combustion, vehicle exhausts, cooking, factory emission gases and the use of asphalt in paving roads that reach the aquatic environment (Dhale *et al.*, 2003).

As a result of the continuous population explosion and the accompanying dumping of industrial and agricultural wastes and the excessive use of energy sources, especially petroleum products, this has led to an imbalance in the ecosystem. Due to the importance of the Shatt Al-Arab River, this study was carried out, which aims to determine the concentrations of total petroleum hydrocarbons in the sediments and to know the effects of the interaction with seasonal changes on them and their relationship to the concentrations of total organic carbon.

Sources and Methods

Sediment samples were collected seasonally from summer 2018 to spring 2019 from five stations on the Shatt Al-Arab River (Al-Qurna, Al-Sharish, Al-Shafi, Al-Deir and Al-Hartha) (Table 1 and Figure 1), using a sediment sampling device (Grab Sampler). They were stored in a refrigerated box until reaching the laboratory, where they were dried, ground, and sieved with a 63 micron sieve to prepare them for measurement.

Table 1. Locations of the sampling sites.

No. of Station	Stations	Locations	
		N	E
1	Al-Qurna	31°00'17.2"	47°25'49.9"
2	Al-Sharish	30°56'58.2"	47°28'28.6"
3	Al-Shafi	30°54'09.8"	47°30'12.1"
4	Al-Deir	30°48'13.2"	47°34'47.5"
5	Al-Hartha	30°44'48.1"	47°41'58.3"

Determination of TPH in sediments:

The method described by Goutx and Saliot (1980) was used to determine the concentrations of hydrocarbons in the sediments. 20 g were taken and placed in a thimble and the hydrocarbons were extracted using a mixture of solvent (methanol:benzene 1:1 v/v) for 48 hours at a temperature not exceeding 40°C.

Then the extract was left to cool and the saponification process was carried out for two hours by adding 15 ml of aqueous potassium hydroxide MeOH(KOH) (4M) at a temperature of 40 °C as well and left to cool. Using a separating funnel, the unsaponified material was separated and passed through the separation column (which is a glass column about 20 cm long; equipped with glass wool at the bottom and above it 2 g of silica gel, 2 g of alumina and 2 g of anhydrous sodium sulfate (Na2SO4), respectively). After adding 25 ml of hexane, then the aromatic part was collected by adding 25 ml of benzene. The total petroleum hydrocarbons concentrations in the samples were measured using a spectrofluorometer (model Shimadzu).

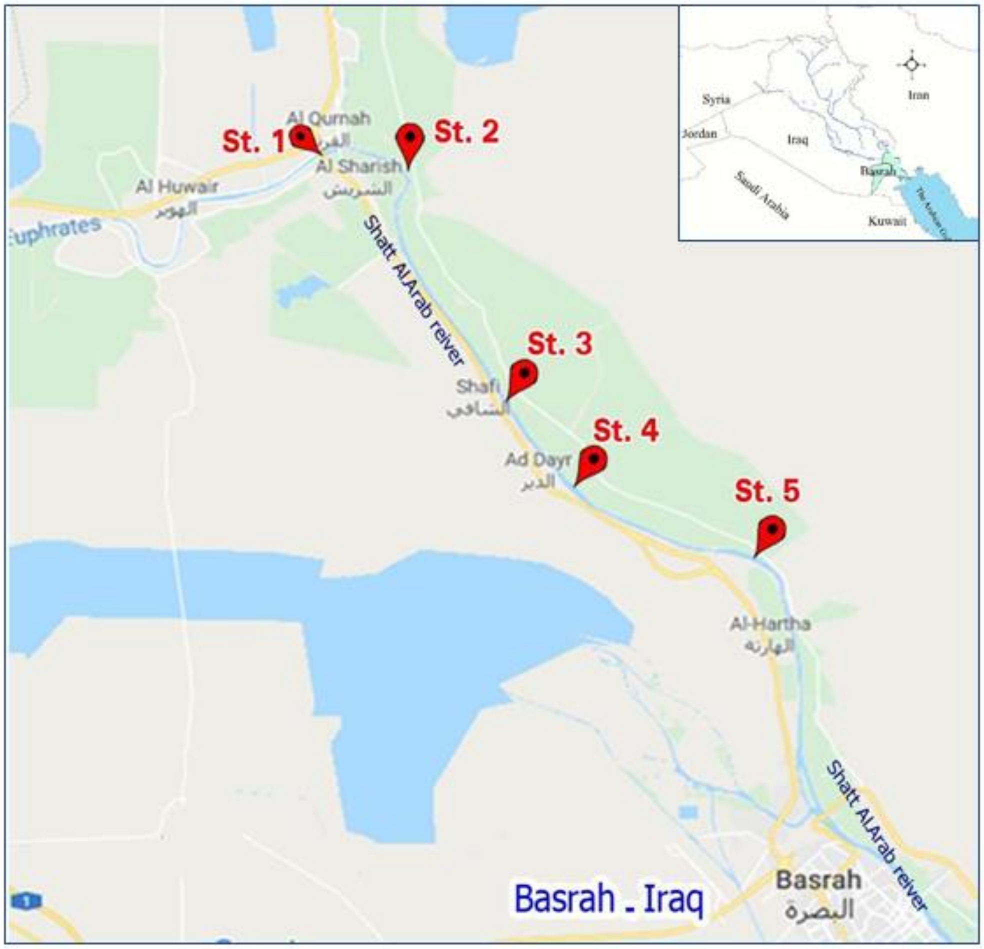

Figure 1: Map of sampling sites.

Grain size analysis (٪):

The analysis of average particle size was carried out in the laboratories of the Department of Marine Sediments at the Marine Sciences Center using the pipette method described by Folk (1974).

Determination of TOC (٪) in sediments:

The furnace method was used to measure the percentage of TOC content in the sediments described by Ball (1964), where 2 g of the sample were placed in the furnace at 550 °C for 48 hours. The result from the difference between the initial weight and the dry weight represents the TOC contents.

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Statistical Analysis:

Data were statistically analyzed using the analysis of variance (ANOVA). Data were collected statistically using the software Minitab Ver.17, at the probability level of $P \leq 0.05$.

Results and Discussion

Total Petroleum Hydrocarbons in the Sediments:

Hydrocarbons reached the aquatic environment from various sources, including biosynthesis by living organisms, especially aquatic plants, or entry from adjacent lands and the atmosphere (GESAMP, 1993).

Total petroleum hydrocarbon (TPH) concentrations in the sediments ranged between 6.593 μg/g dry weight at Al-Shafi station during the summer and 52.793 μg/g dry weight at Al-Deir station during the winter (Figure 2). Statistical analysis showed significant differences between seasons at the probability level $P \leq 0.05$ (RLSD=11.245), while no significant differences were observed between stations at the probability level $P > 0.05$.

The results showed that the highest concentrations of TPH were in Al-Dair and Al-Hartha stations compared to the first station, and the reason for this may be due to the position of the two stations near the oil fields in the Nahran Ommer area on the eastern bank of the Shatt Al-Arab compared to Al-Qurna station, which is far from this location. Also, the high concentrations of hydrocarbons in the sediments are attributed to the biodegradation of dead aquatic plants and phytoplankton by microorganisms in the sediments (Al-Timari *et al*., 2003; Al-Imarah *et al*., 2006).

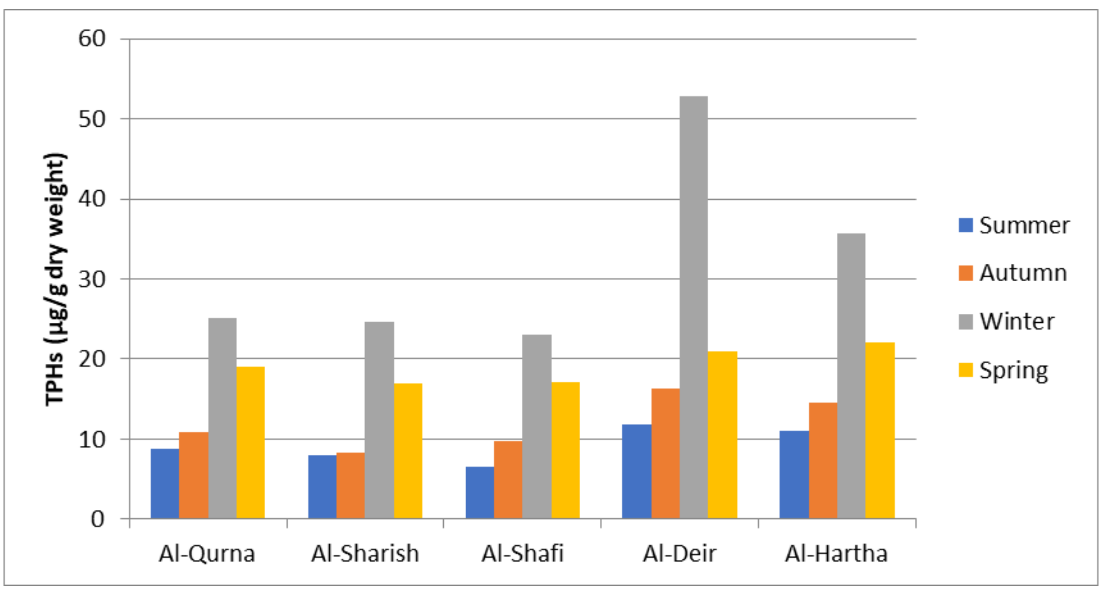

Figure 2: Total Petroleum Hydrocarbons (μg/g dry weight) in sediments of the studied sites at the Northern Part of Shatt Al-Arab River.

Pollutants in the aquatic ecosystem tend to adsorb on the particles and suspended matter in the water column and then sink to the bottom (Al-Hejuje, 2014), so that a small part of hydrocarbons reached the aquatic environment, remains in the river column, while the largest part settles on the bottom sediments (Adeniji *et al.*, 2017), affecting many aquatic organisms in the ecosystem (Farrington and Takada, 2014). The present results are compared with those obtained in the region (Table 2).

Table 2: Concentrations of TPH (µg/g dry weight) in sediments of the present study compared with those of other local studies.

Locations	**Conc. of TPHs (µg/g dry weight)**	**References**
Al-Hawizeh Marsh	0.11-37.02	Al-Khatib (2008)
Shatt Al-Arab River – Northern Part	7.37-24.41	Al-Imarah *et al.* (2010)
Al-Kahla River - Missan	3.16 - 135.18	Jazza (2015)
Shatt Al-Arab Estuary and NW Arabian Gulf	19.43-49.09	Al-Saad *et al.* (2017)
Al-Chibayish Marsh – Thi Qar	2.98-17.98	Al-Atbee (2018)
Shatt Al-Basrah	6.98-5.57	Galo *et al.* (2022)
Shatt Al-Arab River	6.59-52.79	Present Study

Total Organic Carbon (TOC ٪) in the Sediments:

Organic carbon is produced from rock weathering processes, dead remains of plants and animals, as well as various human activities (Hantoush, 2006). Also, Human and animal waste plays an important role in increasing the organic carbon content in the sediments, and the chemical and biological processes that occur in the sediments greatly affect the total percentage of organic carbon (Balasim, 2013).

Total organic carbon (TOC) in the sediments are represented by the amount of organic matter remaining after decomposition, and their value are affected by many factors, including primary productivity, sedimentation rate, amounts of organic detritus resulting from the decomposition of organisms after their death, and the speed of decomposition of organic matter by decomposing organisms (Routh *et al.*, 2004).

The results of the current study showed that the lowest percentage of TOC was 5.754% in Al-Sharish station during the summer and the highest was 15.612% in Al-Hartha station during the winter (Figure 3). The statistical analysis showed significant differences between seasons at the probability level $P \leq 0.05$ (RLSD=2.038), while no significant differences were observed between stations at the probability level $P > 0.05$. These results agreed with some previous results, but their values were higher, as the results of the current study can be compared with their counterparts in the region (Table 3).

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The highest values recorded during winter correspond to the high rate of dead aquatic plants (Al-Atbee, 2018), while the lowest values occurred during summer for all stations and may be attributed to the high temperature stimulating microbial enzymes and thus increases the biodegradation processes of organic matter (Arocena, 2007).

A positive correlation was found between TPH concentrations and the percentage of TOC in the sediments, which is in agreement with many other results who indicated that there is a relationship between the content of hydrocarbons and total organic carbon in the sediments such as Hantoush (2006); Al-Imarah *et al*. (2010) and Jazza (2015).

Hydrocarbons are one of the most important components of organic matter in sediments, and any increase in their concentrations is evidence of an increase in the amount of organic matters and thus an increase in the value of (TOC%) (Massoud *et al*., 1998; Angelo Huang *et al*., 2012).

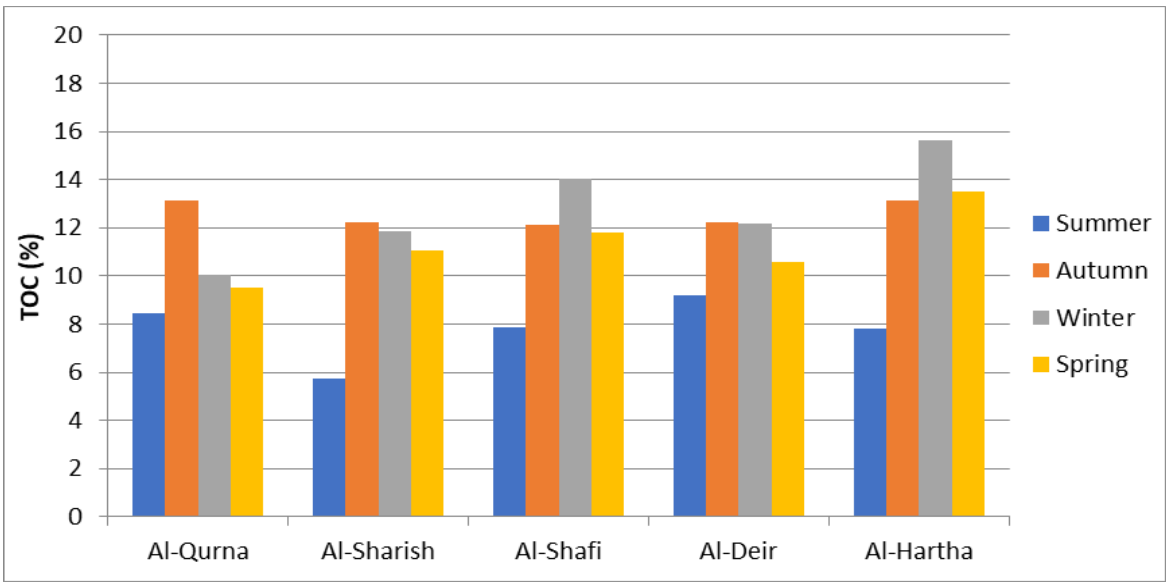

Figure 3: Total Organic Carbon (%) in sediments of various sites at the Northern Part of the Shatt Al-Arab River.

Table 3: Percentages of TOC in sediments of the present study compared with results of other local studies.

Locations	(TOC %)	References
Al-Kahla River - Missan	0.078-0.927	Jazza (2015)
Shatt Al-Arab Estuary and NW Arabian Gulf	0.1-1.34	Al-Saad *et al*. (2017)
Al-Chibayish Marsh – Thi Qar	9.93-13.49	Al-Atbee (2018)
Shatt Al-Arab River	5.754-15.612	Present Study

Grain (Particles) size:

The grain size analysis of sediments indicates the nature of the particles, their texture and their different sizes in the sedimentary material to evaluate the inter-sedimentary deposits (Wasel and Albadran, 2003), and the terms sand, silt and clay refer to the relative size of soil particles (Balasim, 2013).

The results of the present study showed that the lowest percentage of sand was 4% in Al-Hartha station, while the highest percentage was 17% recorded in Al-Shafi station, and the lowest percentage of silt was 51% in Al-Qurna station and the highest percentage was 72% in Al-Deir station, while the lowest percentage of clay was 20% in Al-Shafi station and the highest percentage was 41% in Al-Qurna station (Table 4).

The results of the texture showed that the sediments are silty clay, which means an increase in the accumulation of hydrocarbons in them. There is negative relation between the smaller size of the sediment particles and the accumulation of hydrocarbons compound in them. These results were in agreement with those of Al-Imarah *et al*. (2010).

Table 4: Percentage of texture components of sediments at the Northern Part of Shatt Al-Arab River.

Stations	Texture Components		
	Sand (%)	Silt (%)	Clay (%)
Al-Qurna	8	51	41
Al-Sharish	6	70	24
Al-Shafi	17	63	20
Al-Deir	6	72	22
Al-Hartha	4	65	31

An increase in the proportion of sand was observed in the texture of the sediments at Al-Shafi station, which may be due to the many human activities and paving process of the western bank of Shatt Al-Arab River. According to the proportions of the components of the sediment texture, the Shatt Al-Arab sediments can be considered silty clay sediments, which is in agreement with Al-Hejuje (2014) and Al-Saad *et al*. (2016).

Conclusion:

- Temporal and spatial variations in TPHs concentrations were recorded in the Shatt Al-Arab sediments.
- Hydrocarbon compounds had a positive correlation with total organic carbon content.
- The fourth station in the present study (Al-Hartha) recorded the highest concentrations of TPH in the sediments because that they were directly affected by crude oil extraction and processing in the Nahran Ommer area.

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- The type of grain size of sediments is silt-clay and average of clay (27.6%), silt (64.2%) and sand (8.2%).

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المركبات الهيدروكربونية الكلية وعلاقتها بمحتوى الكربون العضوي الكلي في رواسب الجزء الشمالي لنهر شط العرب البصرة - العراق

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المستخلص

تضمنت الدراسة الحالية قياس تراكيز المركبات الهيدروكربونية النفطية الكلية وتقدير النسبة المئوية للكاربون العضوي الكلي ومكونات النسجة في رواسب خمس محطات اختيرت في الجزء الشمالي من شط العرب وهي (القرنة والشرش والشافي والدير والهارثة) بشكل فصلي من عام 2018 ولغاية عام 2019. قدرت تراكيز المركبات الهيدروكاربونية النفطية الكلية في الرواسب باستخدام جهاز الفلورة فقد بلغ أدنى تراكيزها 7.933 مايكغم/غم وزن جاف في محطة الشافي خلال فصل الصيف وأعلاها 52.793 مايكغم/غم وزن جاف في محطة الدير خلال فصل الشتاء. تراوحت النسبة المئوية لمحتوى الكاربون العضوي الكلي في الرواسب بين (5.754%–15.612%). لوحظ أن نسجة الرواسب من نوع غرينية طينية اذ أن معدل نسبة الطين (27.6%) والغرين (64.2%) والرمل (8.2%). أظهر التحليل الإحصائي وجود علاقات ارتباط موجبة بين كل من تراكيز المركبات الهيدروكابونية النفطية الكلية والكاربون العضوي الكلي في الرواسب.

الكلمات المفتاحية: إجمالي الهيدروكربونات النفطية، إجمالي الكربون العضوي، نسيج الرواسب، نهر شط العرب.