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Total Petroleum Hydrocarbons in the water and sediment of Tigris, Euphrates and Shatt Al-Arab Rivers

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Abstract

The total petroleum hydrocarbon (TPHs) content in the water and sediments was assessed because of its widespread distribution in the environment. Petroleum hydrocarbons are pollutants that contain a variety of hazardous organic compounds, many of which can mutate and exert cancerous effects on humans. Water and sediment samples were collected from three locations along the Tigris, Euphrates, and Shatt Al-Arab rivers from the period Oct.,2022 to July., 2023. The results showed that TPHs in water range from 0.03 µg/l to 0.09 µg/l. while TPHs in sediments is range from 3.82 µg/g dry weight to 20.13 µg/g dry weight. Sediments act as sinks for pollutants; therefore, they have the highest concentration of TPHs compared to water. A negative correlation was observed between TPHs in water and water temperature or pH. In sediments, a negative correlation was found between TPHs and the clay percentage.

Keywords: Total petroleum hydrocarbons, TPHs, sediments, Tigris, Euphrates, Shatt Al-Arab River.

Introduction

Environmental concerns are significant to humanity (Wang & Yang, 2016). Organic and inorganic pollutants enter river basins with polluted wastewater, effluent discharge, stormwater runoff, and air deposition (Al-Hejuje *et al*.,2015a; Abdel-Shafy and Mansour, 2016; Lee *et al*. 2020).

Water pollution is defined as changes in the physical, chemical, and life characteristics of water directly or indirectly caused by human intervention through the introduction of unwanted materials or energy sources into the aquatic environment, causing disturbance or imbalance in the ecosystem, which adversely affects the living environment and human existence. Global population growth has led to increased water demand and pollution (Fang,2019). Moreover, low-to-moderate pollution poses a threat to humans and aquatic organisms (Edori,2019).

River sediments provide excellent repositories for various organic and inorganic contaminants (Eker 2020). Sediment contaminants may decrease or eradicate any kind with commercial, recreational, or environmental significance, either via direct impact or by influencing the food supply required by inhabitants. Thus, polluted sediments may have fatal and sub-fatal effects on benthic organisms (sediment residents) and other sediment-related organisms (Spellman, 2017).

The total petroleum hydrocarbons (TPHs) content of water is the most important criterion for evaluating the relationship between water, oil, and gas deposits. Recently, analysis of these compounds in water has been used in petroleum exploration. Organic matter (OM) plays a crucial role in aquatic systems by affecting biochemical processes, nutrient cycling, biological availability, and chemical reactions (Niemirycz *et al*. 2006). Chemical interactions in the organic residue caused by suspended organisms are the primary source of pollutants entering water (O'Connell *et al*., 2000). Furthermore, surface sediments in rivers represent a sink for hydrocarbons, and this accumulation of hydrocarbons in sediments could serve as a source of water pollution in the event of changes in environmental conditions (Al-Hejuje *et al*., 2015a). Because they are highly nutritious, they undergo degradation by microorganisms (Arzayus & Canuel, 2005). Once these organisms die, they settle at the bottom and are exposed to chemical and bacterial degradation (Krishnanandan and Sriwafastmy 2013; Krishanamurthy 2020; Mirahmadi Babaheydari 2021).

The aim of this study was to determine the total petroleum hydrocarbons (TPHs) in the water and sediments of the Tigris, Euphrates, and Shatt al-Arab Rivers to assess the concentrations, distributions, and sources of these pollutants.

Materials and Methods

The study was conducted between October 2022 and July. 2023. The studied sites were represented by three stations on the Tigris, Euphrates, and Shatt Al-Arab Rivers (figure 1).

Water samples were collected from stations at least 20 -30 cm under the water surface using dark glass bottles and preserved in situ with 40 ml chloroform. Samples were not collected during the rainy season. Hydrocarbons in the water samples (approximately 5 L) were extracted according to (UNEP,1989) by mixing with chloroform (40 ml) for 30 min. using an electric mixer, the liquid was drained and the remaining 1 liter was transferred to a separating funnel. The separating funnel was shaken manually for 15 min and separated into two layers. The organic phase (lower layer) was carefully passed through a glass column containing glass wool and (5 g) anhydrous sodium sulfate (Na_2SO_4, 5 g), and the sample was collected in a 100-mL glass beaker and air-dried. The sample was then dissolved in n-hexane (5 ml) and passed through a 20 cm long glass column (packed with glass wool at the bottom). A layer (10 g) of silica gel, particle size (100-200), and 10 g of alumina (Al_2O_3), particle size (100-200) and 5 g of anhydrous sodium sulfate (Na_2SO_4) on the top). The aliphatic fractions were extracted from the column using n-hexane (25 mL), while the aromatic fractions were extracted with benzene (25 mL). The aromatic fractions were air-dried and stored until detection using a fluorometer to measure total petroleum hydrocarbons (TPHs).

Sediment samples were collected from three stations, dried at the laboratory temperature, ground, and sieved (<63 µm). Twenty grams of ground sediment were placed in a cellulose thimble. The sample was placed in a Soxhlet

Extraction device, and hydrocarbon compounds were extracted according to a previously described method (Goutx & Saliot, 1980) using 120 ml of a mixture of Methanol: Benzene (1:1) for 48 h at temperatures below 40 °C. Saponification was then performed for two hours by adding (15 ml) of a mixture of methanolic potassium hydroxide (4M $KOHCH_3CH$) at the same temperature, and the extract was cooled to room temperature. (50 ml) n-hexane was added to the sample in the separating funnel, and the sample was shaken manually for 15 minutes, then the funnel was left to separate two layers. The bottom layer was discarded, and the top layer (hexane with hydrocarbons) was passed through a separating column containing glass wool at the bottom, silica gel, alumina, and anhydrous sodium sulfate. Normal hexane (25 ml) was added to obtain the aliphatic fraction, followed by benzene (25 ml) to obtain the aromatic fraction. The aromatic fractions were evaporated at laboratory temperature, and then (3 ml) of n-hexane was added to prepare the sample for measurement by a fluorescent device to measure total hydrocarbons.

Basrah Regular Crude Oil used as a standard. Spectrofluorometry at 360 nm emission intensity and 310 nm excitation with monochromatic slits of 10 nm was used to quantify the total petroleum hydrocarbons in the extracted water and sediment samples.

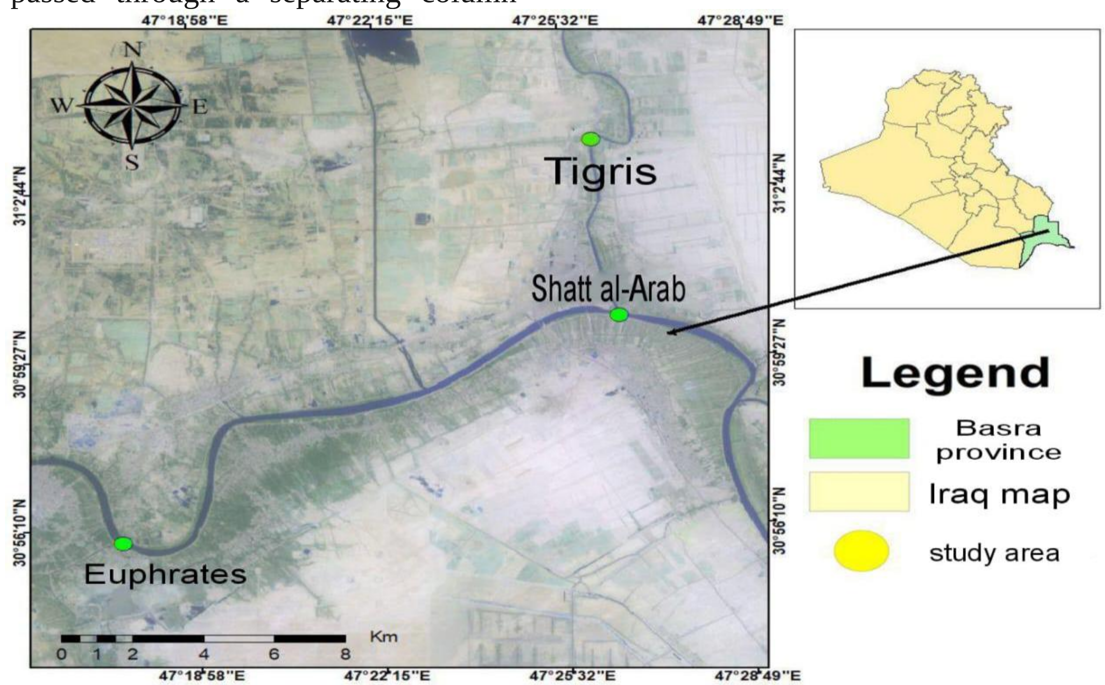

Fig. (1) Study stations.

Results and discussion

The results are represented seasonally; two months make one season (October and November) represent the autumn season; (December and January) represent the winter season; (March and April) represent the spring season; and (June-July). represents the summer. Some of the water variables recorded at the stations studied are listed in Table 1.

Table (1): Water variables at the studied stations.

Station	Season	Water variables				
		Temp.	pH	EC(µS/cm)	TDS(mg/l)	Turb.(NTU)
Tigris	Autumn	32±2.83	9.69±0.63	469.5±212.84	746±698.62	-
	Winter	13.9± 0.57	8.13±1.45	1051±1267.14	572.5±338.70	19.15±16.69
	Spring	24.25±4.60	9.34±0.01	2313±57.98	1140.5±7.78	10.77±0.05
	Summer	36.5± 4.95	9.40±0.10	1705±134.35	756±231.93	23.26±21.29
Shatt Al-Arab	Autumn	34±2.83	9.64±0.28	431±258.80	676.5±539.52	-
	Winter	14.8±0.99	8.48±1.38	1644±982.88	1507.5±477.30	8.58±0.86
	Spring	25±4.24	9.41±0.06	2283±173.95	992.5±406.59	9.42±5.61
	Summer	36±7.07	9.50±0.07	1010±1195.01	882±80.61	9.50±0.85
Euphrates	Autumn	35.5±2.12	9.68±0.11	419.5±71.42	771.5±1016.11	-
	Winter	15.5±0.71	8.75±1.20	820±35.36	958.5±1076.92	5.99±0.11
	Spring	24±7.07	9.22±0.23	3165±233.35	1577±120.21	5.89±2.40
	Summer	36.5±9.19	9.50±0.14	1601±376.18	956±29.70	8.85±4.45

TPHs in water:

The concentrations of total hydrocarbon compounds in water samples recorded the highest value (0.89) µg/L at the Shatt Al-Arab station during winter, and the lowest value (0.013) µg/L at the Euphrates stations during summer (Figure 2). The results of the statistical analysis using the one-way analysis of variance (one-way ANOVA) test showed that there were significant differences ($p<0.05$) according to the seasons, with the highest values recorded during winter and the lowest values recorded during summer, whereas there were no significant differences ($p>0.05$) between the stations.

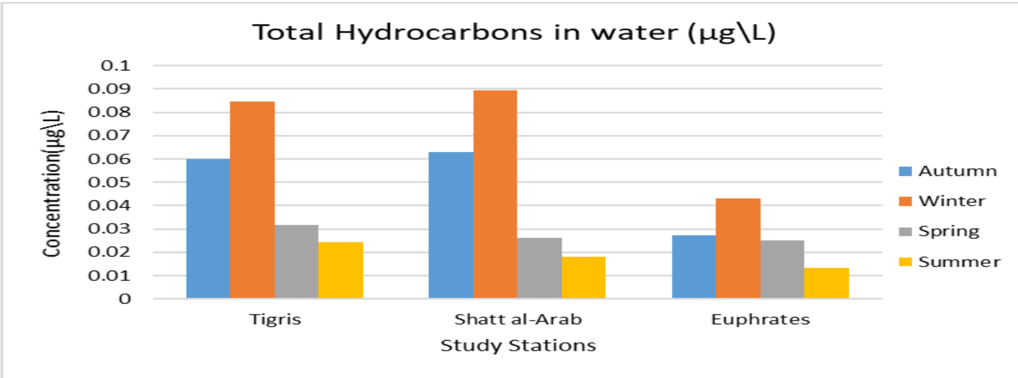

Fig. (2) Total petroleum hydrocarbons (TPHs µg/L) in water at the study stations.

TPHs in sediments:

The concentrations of total hydrocarbon compounds in sediment samples recorded the highest value (20.13) µg/L at the Shatt Al-Arab station during the winter season and the lowest value (3.82) µg/L at the Euphrates station during the summer season (Figure 3). The results of the statistical analysis using one-way analysis of variance (one-way ANOVA) showed that there were no significant differences ($p>0.05$) according to station, but there were significant differences ($p\leq0.05$) according to season. The highest rate was recorded in winter, whereas the lowest rate was recorded in summer.

The TOC content and sediment texture were also determined (Table 2).

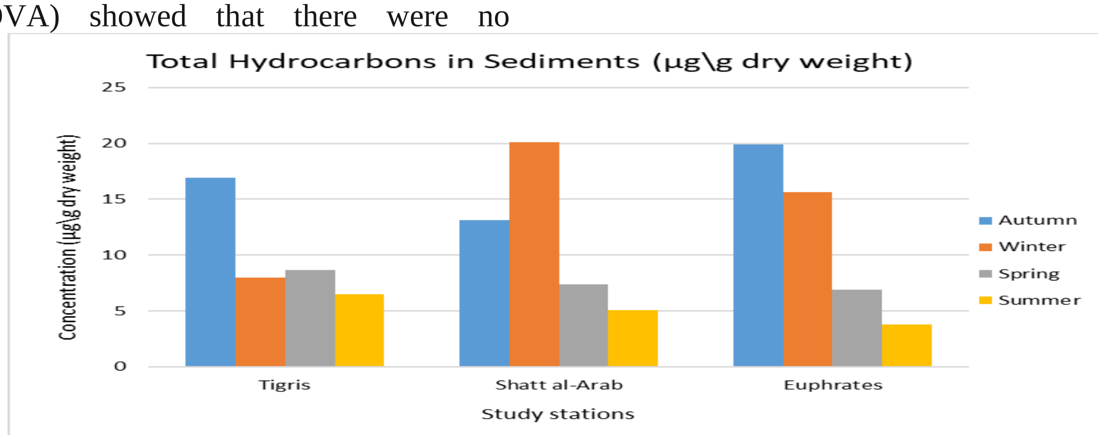

Fig. (3) Total petroleum hydrocarbons (TPHs µg/g dry weight) in the sediments of the studied stations.

Table 2: Total organic carbon (TOC%) and sediment texture at the studied stations.

Station	Season	Sediments			
		TOC%	Sand%	Silt%	Clay%
Tigris	Autumn	9.69±0.05	17±1.41	49±9.90	34±8.49
	Winter	8.12±0.05	4.5±2.12	74±2.83	21.5±4.95
	Spring	9.51±0.98	9±0	73.5±17.68	17.5±17.68
	Summer	9.65±1.22	8.5±2.12	33±14.14	58.5±16.26
Shatt Al-Arab	Autumn	9.28±0.46	8.5±7.78	69±4.24	22.5±3.54
	Winter	8.69±1.14	23.5±2.12	62.5±7.78	14±5.66
	Spring	9.60±0.46	13±15.56	72±29.70	15±14.14
	Summer	9.05±0.07	16±1.41	43±0	41±1.41
Euphrates	Autumn	8.00±0.24	12.5±3.54	63.5±2.12	24±1.41
	Winter	7.97±0.35	16±14.14	67.5±12.02	16.5±2.12
	Spring	7.62±1.45	7.5±2.12	64±5.66	28.5±7.78
	Summer	8.42±0.36	17.5±3.54	22.5±20.51	62±21.21

TPHs in water: The lowest levels of TPHs in water compared to sediments could be attributed to the photo-oxidation, evaporation, and biodegradation of petroleum hydrocarbons that occurred along the water column. Sedimentation processes also contribute to an increase in the concentration of petroleum hydrocarbons in the sediments (Al-Hejuje *et al*., 2015 b). Most previous studies have shown that intense solar radiation coupled with relatively high water temperatures is a characteristic feature of the climate in the subtropical region of Iraq (Moyel, 2010). These two factors could account for the low levels of dissolved hydrocarbons in water.

The results showed that the highest levels of TPHs in water were recorded during winter, whereas the lowest levels were observed during summer, which is consistent with (Al-Atbee,2018). This result may be due to the temperature required for the removal of most hydrocarbons from water. Temperatures affect two main directions. The first is to increase evaporation, in which carbon compounds with low molecular weights evaporate, as well as to break down carbon compounds with high molecular weights (Law, 1981). The second effect of temperature is the increase in the enzymatic activity of microorganisms that use oil as an important source.

In addition, high levels of TPHs were observed during winter, which may be attributed to rainfall from the atmosphere polluted with these compounds which occur during winter. In addition, using a large amount of wood and hydrocarbon compounds for heating or other uses during the winter season produces high levels of hydrocarbon compounds (Al-Atbee,2018). The results of this study agree with those of

Al-Khatib (2008) and Jazza (2015), who found a significant negative correlation between TPHs and temperature and pH ($r=-0.468$ and $r=-0.440$ at $p<0.05$), respectively.

The total petroleum hydrocarbons (TPHs) in sediments are organic compounds that are toxic environmental pollutants (Al-Halfy *et al*. 2021). The distribution of petroleum hydrocarbons in surface sediments plays an important role in oil pollution and in understanding the temporal variations in aquatic environments (Al-Hejuje,2014). The high TPHs concentrations in the sediments compared with those in the water column may be due to the high sedimentation processes occurring along the river. The present results agree with those of Aziz (2005), who found that sediments accumulate more hydrocarbons than water because of their high capacity for adsorption.

Results of the present study showed the highest levels of TPHs in sediment during winter, while the lowest levels observed during summer, this may be due to the climate which is hot and dusty in summer that lead to increase the deposition of compounds from atmosphere to sediments (Al-Rudaini *et al*., 2019), A negative significant correlation between TPHs and Clay percentage in sediments texture ($r=-0.416$ at $p<0.05$).
Compared to previous studies on the Iraqi Rivers (Table 3), the recorded concentrations of total petroleum hydrocarbons were within the limits.

Table 3: Comparison of TPHs in water and sediments in the present study (Tigris, Shatt al-Arab, and Euphrates Rivers) with other studies in the Iraqi Rivers.

Study area	**TPHs in water(µg/L)**	**TPHs in sediments (µg/g)**	**Source**
SHATT AL-ARAB ESTUARY	2.03-19.58	10.15-30.16	(Mahdi,2015)
Tigris River	-	4.05- 128.28	(Al- Nakeeb, 2015)
Shatt Al Arab	5.18-37.59	4.76-45.24	(Al-Hejuje , 2015)
Shatt Al Arab Estuary and North-West Arabian Gulf	3.09-30.87	19.43-49.09	(AL-Saad *et al*.,2017)
some rivers in Misan province	0.038-0.074	31.35-96.13	(Jazza,2017)
Euphrates River	8.43-31.28	118-205	(AL-Taher *et al*.,2020)
Tigris River, Maysan Province, Southern Iraq	2.85-5.22	-	(Lazim,2021)
Abu Al-Khasib River	13.49-19.89	91.84-107.44	(Al Tamimi,2021)
Shatt Al Arab, Tigris, Euphrates	-	1.39-10.83	(Salem *et al*.,2022)
Tigris, Shatt Al Arab, Euphrates	0.03-0.09	3.82-20.13	Current Study

Conclusion

The total petroleum hydrocarbon contents from the Tigris, Euphrates, and Shatt Al-

Arab Rivers indicate evidence of crude oil contamination in the water and sediments. TPH levels may have serious health implications; therefore, epidemiological studies of indigenous people in the closest area are imperative. It is recommended that oil fingerprinting be carried out to identify pollution sources and provide cost-effective remediation measures if adverse health defects are to be prevented.

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تراكيز المركبات الهيدروكربونية النفطية الكلية في مياه ورسوبيات أنهار دجلة والفرات وشط العرب

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المستخلص:
تم تقييم إجمالي محتوى الهيدروكربونات النفطية (TPHs) في المياه والرسوبيات بسبب انتشارها على نطاق واسع في البيئة، والهيدروكربونات النفطية هي ملوثات تحتوي على مجموعة متنوعة من المركبات العضوية الخطرة، والعديد منها لديه القدرة على التحور ولها تأثيرات سرطانية على الإنسان .تم جمع عينات المياه والرسوبيات من ثلاثة مواقع على أنهار دجلة والفرات وشط العرب للفترة من تشرين الاول 2022 إلى تموز 2023. وأظهرت النتائج أن إجمالي الهيدروكربونات النفطية في المياه يتراوح من 0.01 ميكروغرام / لتر إلى 0.11 ميكروغرام/ لتر. بينما تتراوح الهيدروكربونات النفطية في الرسوبيات من 2.46 ميكروغرام/غرام من الوزن الجاف إلى 26.21 ميكروغرام/غرام من الوزن الجاف .تعمل الرسوبيات كخزان للملوثات، وبالتالي فهي تحتوي على أكبر تركيز من الهيدروكربونات النفطية مقارنة بالمياه .تم تسجيل علاقة ارتباط سلبية بين الهيدروكربونات النفطية في المياه مع درجة حرارة المياه أو الاس الهيدروجيني. وفي الرسوبيات وجد ارتباط سلبي بين تراكيز الهيدروكربونات النفطية ونسبة الطين في الرسوبيات.
الكلمات المفتاحية: الهيدروكربونات النفطية الكلية، الهيدروكربونات النفطية، الرسوبيات، دجلة، الفرات، نهر شط العرب.