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TOC and TPH Relationships in Khor Al-Zubair Sediments: Hubungan TOC dan TPH dalam Sedimen Khor Al-Zubair

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Abstract

General Background Total petroleum hydrocarbons are persistent contaminants in marine sediments and are closely associated with organic matter. **Specific Background** Total organic carbon is widely used as an indicator of sedimentary processes and hydrocarbon retention. **Knowledge Gap** However, limited studies have evaluated the vertical and spatial relationship between TOC and TPHs in sediment cores from Khor Al-Zubair. **Aims** This study aimed to determine the distribution of TOC and TPHs and assess their relationship in sediment cores collected from five stations in Khor Al-Zubair, southern Iraq. **Results** TOC values ranged from 0.058% to 0.193%, while TPH concentrations ranged from 0.2894 to 12.4434 µg/g, with higher values generally recorded in surface layers and at Station 5. Correlation analysis revealed variable relationships between TOC and TPHs, including strong positive correlations at most stations and a strong negative correlation at one station. **Novelty** This study provides station-specific insights into contrasting TOC–TPH relationships within a single lagoon system. **Implications** The findings highlight the role of organic matter and local environmental conditions in controlling hydrocarbon distribution and support the use of TOC as an indicator of sedimentary hydrocarbon retention.

Keywords: Total Petroleum Hydrocarbons, Total Organic Carbon, Sediment Cores, Khor Al-Zubair, Marine Pollution

Key Findings Highlights:

1. Concentrations varied vertically with higher values near sediment surfaces.
2. Organic matter showed contrasting associations across sampling locations.
3. Spatial patterns reflected localized anthropogenic activities.

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Introduction

Hydrocarbons are organic molecules consisting exclusively of hydrogen and carbon. They take up the largest proportion in oil and can account for 80-90% of its total amount [1]. Because hydrocarbons have low solubility in water, the suspended particles in the water column serve as a substate to which they tend to be adsorbed. These particles eventually fall to the ground, and as they do so they work to turn sediments into sinks for contaminants. Toxicokinetics A major concern with these organics pollutants is that they have the potential to bioaccumulate in aquatic organisms [2]. Total petroleum hydrocarbons, or TPHs, refer to all extractable petroleum hydrocarbons. They can be defined as a blend of many different hydrocarbons which vary significantly in size and structure, such as alkanes, alkenes, cycloalkanes, and aromatics, and which range in molecular size from 6 to over 35 carbon atoms [3]. Total petroleum hydrocarbons (TPH) may also be found in small amounts within plants and animals. Primarily, TPH is a group of hydrocarbons which contain carbon (C) and hydrogen (H) atoms, and are known to be hydrophobic, meaning TPH are less likely to dissolve in water [4]. The presence of total petroleum hydrocarbons (TPH) can have negative effects on an aquatic ecosystem by altering water quality, disrupting ecological balance, altering degradation of pollutants, and contaminating potable water sources [5]. There are also varying properties of petroleum that are influenced by the geology and geographic location of the crude oil, as well as the cracking procedures used during refinement [6].

Petroleum spills are major hazards to marine organisms due to possible physiological changes and changes in foraging behavior which can increase mortality and/or decrease health [7]. The impacts of TPH pollution depend on both the concentration of the pollution and the distance from the region of pollution. Additionally, TPH can emit toxic trace organic elements contained in crude oil and crude oil products such as, but not limited to, benzene, toluene, methylene chloride, and chloroform. These trace organic elements are highly soluble in water taking into account human dermal absorption [8] : therefore, chronic exposure levels, which may be fairly low in concentration of water and/or sediment, may or may not affect human health and wellbeing [4]. Total organic carbon (TOC), which is associated with sediments, indicates changing processes in depositional environments, represents ecosystems in historical time and space and provides information which reflects the interconnectedness of biological, chemical and physical processes that occur in sediments; making TOC a useful tool in geology and environmental studies [9]. Ultimately, the aims of this study is to measure pollution concentration based on total organic carbon and total hydrocarbons, and assess the relationship between TPH and total organic carbon.

Study Area

Khor Al-Zubair is a significant location in Iraq located in the northwestern Arabian Gulf. The Khor Al-Zubair is very important for both the state and the nation, being economically important, maintaing a growing industrial base, fisheries, and oil transport [10] . As for the geology of the area, several geological structures are underlain by Quaternary deposits primarily consisting of clay, silt, and sand. Khor Al-Zubair is the largest prominent lagoon in the northern Arabian Gulf [11] , and is approximately 60 km long, with navigable channels having depths of around 10m to 20m. There are many shallow and irregular tidal marshes at the north end of the creek, whose geometrics are complex, similar to the branches of a tree [10] . (Figure 1)

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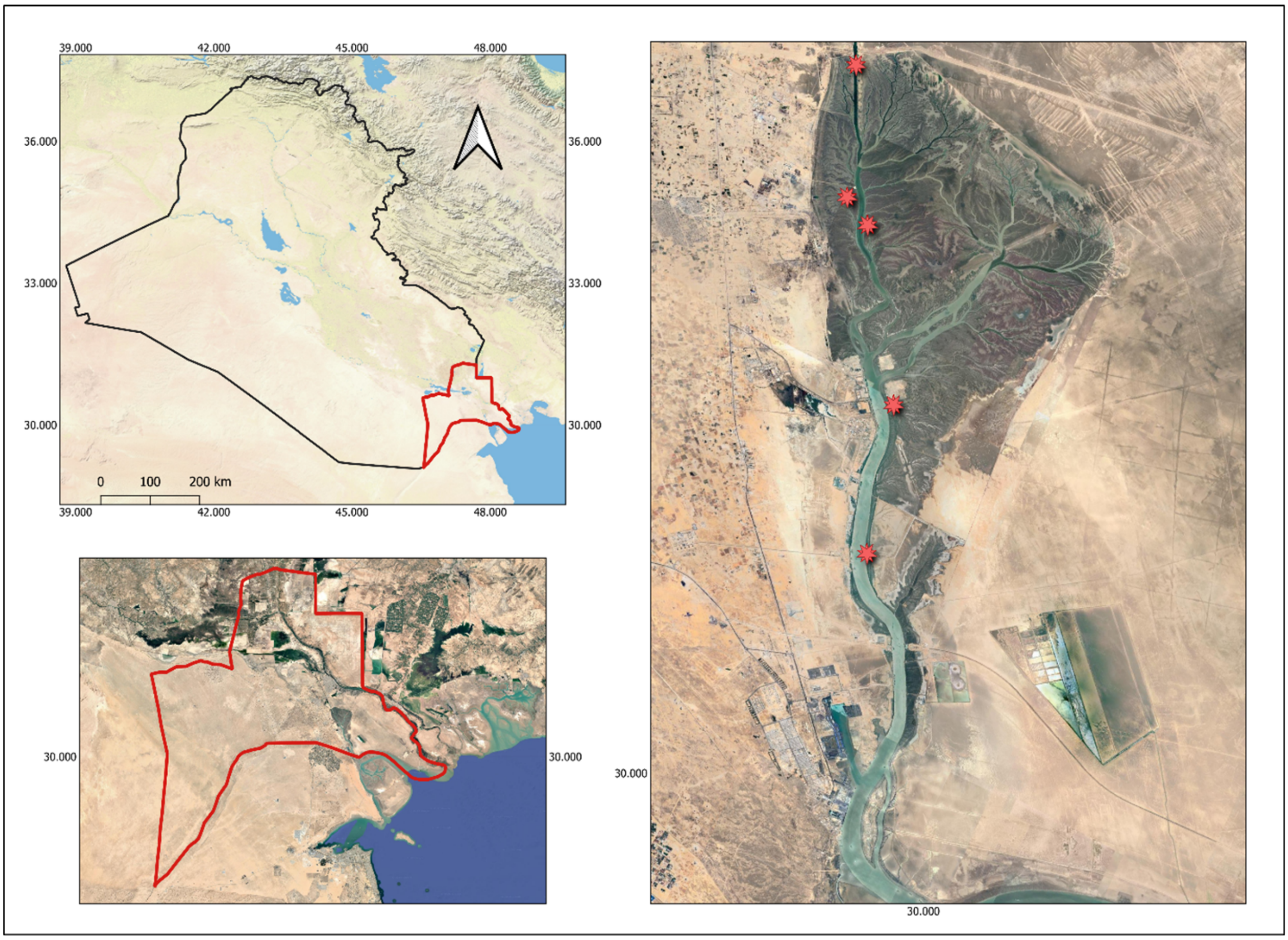

Figure 1. Figure 1: Location of Study Area and Sampling Stations, Southern Iraq.

Materials and Methods

Five sediment core samples were obtained at different locations that represent specific sites within the Khor Al-Zubair area with regards to both assessment and estimation of hydrocarbon variances. Subsequently, the dried sample was initially mixed together using a mechanical grinder to achieve fine powder followed by sieving through a 63 µm mesh to achieve a more constant grain size.

Measurement of Total Petroleum Hydrocarbons (TPHs)

The extraction and analysis of hydrocarbons followed the methodology of Goutx and Saliot 1980. An exact amount of 50 g of dried, ground, and sieved sample sediment was used, and placed in a thimble for the Soxhlet apparatus for intermittent extraction. The extract was made free of elemental sulfur by the addition of activated copper. After, 150 mL of solvent, containing a mixture of methylene chloride and methanol (3:1, v/v), was added to the sediment sample. Before the extract was passed through a column which was packed in this order on the bottom of the column, glass wool, 5 g of silica gel, 2 g of alumina to remove residual fatty acids, and then 2 g of anhydrous sodium sulfate to capture remaining moisture. A standard for crude was used to create standard solutions. Near the 0.003 g weight of crude oil was solubilized for stock in a 10 mL tube with analytical n-hexane. This solution was used as the calibration standard for the determination of TPHs in the extracted sediment samples. TPH concentrations were measured using a Shimadzu RF-530 spectrofluorometer at an excitation wavelength of 310 nm and an emission wavelength of 360 nm and with monochromator slit widths of 10 nm [12].

Measurement of Total Organic Carbon (TOC%)

For the determination of total organic carbon (TOC%), the combustion method described by Ball 1964 was employed. Prior to analysis, all sediment samples were finely ground and passed through a 63 µm sieve to ensure homogeneity and consistency in particle size. A clean crucible was oven-dried and weighed accurately. Subsequently, approximately two grams of the prepared sediment were placed into the crucible and subjected to ignition at 550 °C for 48 hours. After combustion, the crucibles were transferred to a desiccator and allowed to cool to ambient temperature to achieve equilibrium with the surrounding environment. They were reweighed several times until a constant mass was obtained [13]. The TOC content was calculated based on the difference in weight before and after combustion using the following formula:

TOC % = (W2-W3/W2-W1) *100%

where:

W_1 represents the weight of the empty crucible,

W_2 is the combined weight of the crucible and sediment sample before ignition, and

W_3 is the weight of the crucible with the residue after combustion.

Results and Discussion

Table 1 and figure 2 shows the percentages of total organic carbon for the study area, the lowest percentage of total organic carbon was recorded at 0.058 at a depth of 10-15 cm in the third station , and the highest percentage reached approximately 0.193 at a depth of 0-5 cm in the fifth station.

Table 2 and figure 3 shows the concentrations of total hydrocarbon compounds in stations concentrations increased at the shallowest depth of 0-5 cm about 12.1586 . The highest total hydrocarbon concentrations were recorded at station 5, specifically at a depth of 5-10 cm about 12.4434 , while the most significant decrease in concentrations was observed at station 3, at a depth of 45-50 cm about 0.2894.

The results of the correlation coefficient in the stations are :

Station 1 - TPHs and TOC%: There is a very weak positive relationship (r = 0.006), indicating no significant correlation.

Station 2 - TPHs and TOC%: A strong negative relationship (r = -0.893) reflects decreasing TPH concentrations as organic matter increases.

Station 3 - TPHs and TOC%: A moderate positive relationship is noted (r = 0.640).

Station 4 - TPHs and TOC%: A moderately positive relationship is seen (r = 0.776).

Station 5 - TPHs and TOC%: There is a strongly positive relationship (r = 0.859).

Stations	TOC%										Average
Depth	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	45-50	
Core 1	**0.156**	**0.102**	**0.092**	**0.076**	**0.130**	**0.119**	**0.133**	**0.147**	**0.078**	**0.076**	**0.1128**
Core 2	**0.149**	**0.145**	**0.131**	**0.150**	**0.161**	**0.158**	**0.150**	**0.171**	**0.167**	**0.161**	**0.1553**
Core 3	**0.076**	**0.071**	**0.058**	**0.091**	**0.082**	**0.096**	**0.120**	**0.149**	**0.098**	**0.074**	**0.0883**
Core 4	**0.166**	**0.159**	**0.156**	**0.174**	**0.152**	**0.141**	**0.148**	**0.125**	**0.116**	**0.102**	**0.1439**
Core 5	**0.193**	**0.186**	**0.182**	**0.153**	**0.167**	**0.166**	**0.159**	**0.148**	**0.138**	**0.106**	**0.1598**

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Figure 2. Table 1: Total Organic Carbon Percentage in sediment cores.

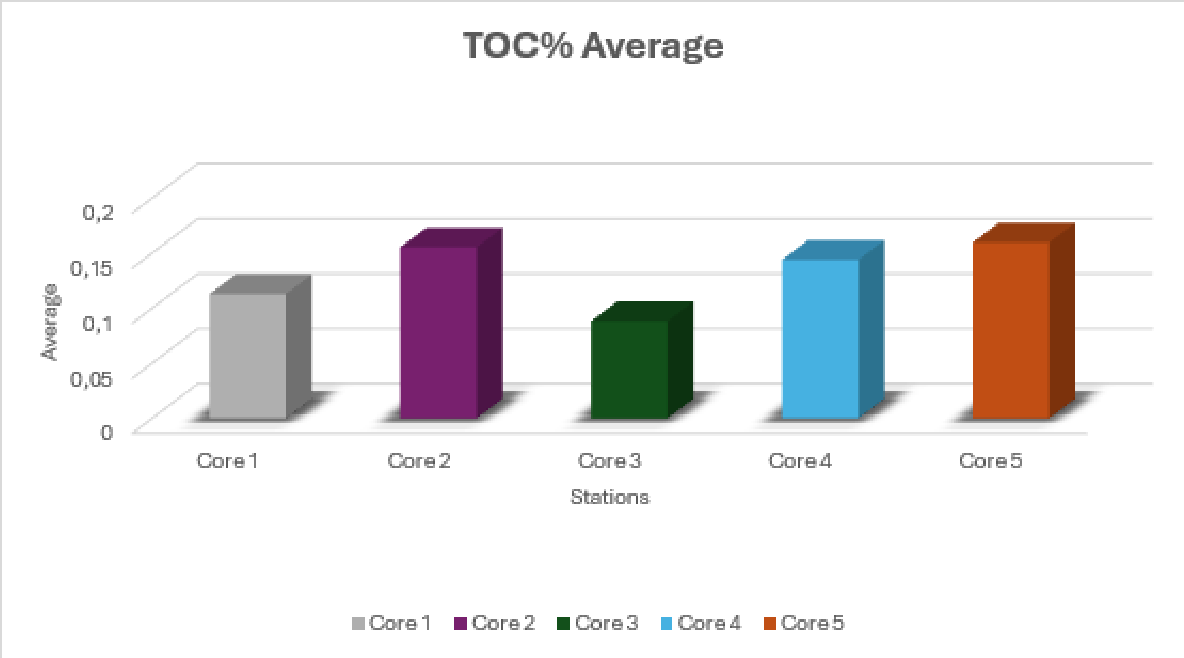

Figure 3. Figure 2: Total Organic Carbon Average in study stations.

Depth	TPHs				
	Station 5	Station 4	Station 3	Station 2	Station 1
0-5	12.1586	5.6244	0.7656	1.7708	2.0556
5-10	12.4434	4.083	1.1174	1.62	4.6862
10-15	11.321	4.8872	1.3856	1.9886	2.441
15-20	9.746	3.6138	0.7656	1.5028	2.2232
20-25	9.4946	3.329	0.5812	1.4358	2.1394
25-30	8.5396	2.7258	0.8828	1.2012	1.7209
30-35	4.485	3.128	0.531	0.8326	1.3184
35-40	4.1668	2.508	0.3132	0.3634	1.1007
40-45	3.6306	2.374	0.2894	0.8828	0.7992
45-50	3.1555	2.1394	0.3802	0.7872	0.6484

Figure 4. Table 2: Concentrations of TPHs (µg/g) dry weight in the sediment of study area.

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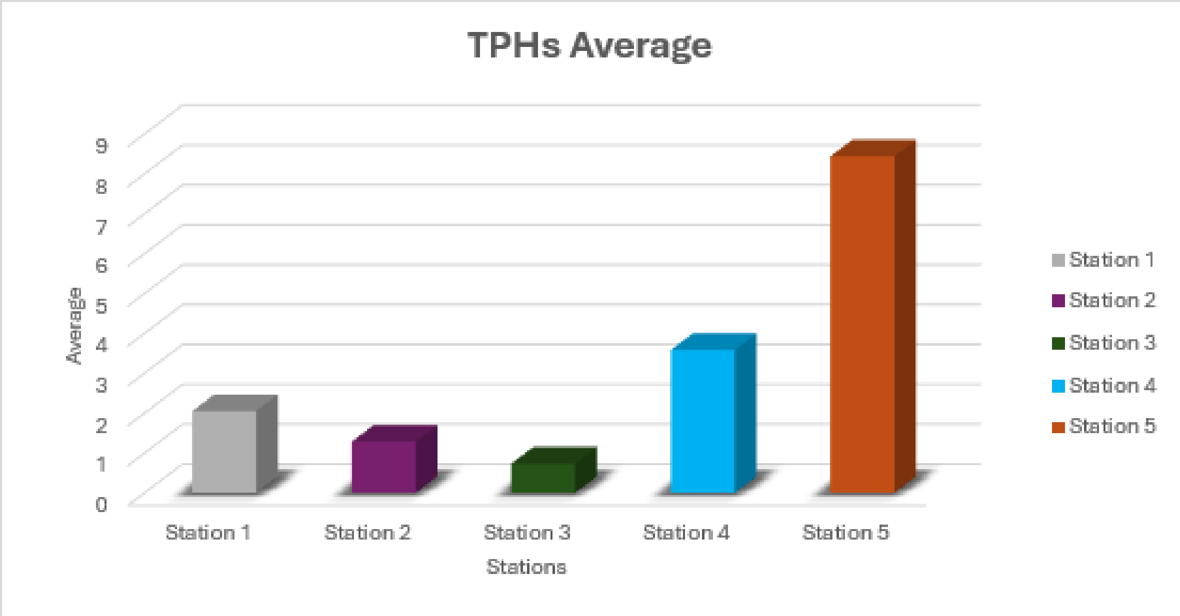

Figure 5. Figure 3: Total Petroleum Hydrocarbon Average in study stations.

Most of the values of TOC are decreased gradually as depth increased. This means that lower concentrations of TOC are typically found in the deeper depths. The primary reason for this trend is that the upper layers of sediment contain a higher concentration of organic materials [14]. Excess TOC in the marine environment may be a result of a combination of an excess of plant debris combined with anthropogenic input. Elevated organic carbon concentrations are often associated with recurring algal blooms in the upper water column largely induced by nutrient enrichment of nitrogen and phosphorus. In heavily populated areas along the coast, anthropogenic inputs from pathways such as stormwater can cause serious and at times, ecologically disruptive events [15].

Khor Al-Zubair has a well-documented record of anthropogenic historical activities contributing to Total Petroleum Hydrocarbon (TPH) contamination. This pollution originates primarily from land-based sources and additional human intervention [8]. The southern region of Iraq, south of the Al-Faw Peninsula and into the eastern Arabian Peninsula, possesses a major oil refinery; one of the primary discharge channels of the oil refinery is the Al-Zubair channel—this channel carries treated waste to the Arabian Gulf. The area has intense marine traffic including oil tankers and crew transfer activity that provide the transport of petroleum from refineries to oil fields and offshore and marine industries. The extent of human activities in the marine environment is an important contributor of hydrocarbon residues to the environment. Added to the marine activities, industrialization and urbanization in connected urban areas has created yet another layer of nuisance light pollution, with potential impacts on sedimentation as well as the adverse impacts on aquatic organisms [16].

The study showed that the pollution levels increased as sampling sites approached 4 and 5, which is likely due to the fact that the port an area historically known to introduce higher pollutant levels from vessels and vessel activity, was located nearby. Table 2 shows the change in concentration for different pollutants and their general trend, specifically noting that the 5th sampling station had a higher presence of pollution compared to the 3rd sampling station.

The relationship between Total Organic Carbon (TOC) and Total Petroleum Hydrocarbons (TPH) indicated a strong positive slope at most sampling stations, meaning sites that have higher concentration of organic carbon would also have higher sedimentary hydrocarbons. The response is often interpreted to be attributed to relatively strong bonding of organic matter with hydrophobic compounds to allow for the adsorption or bonding of hydrocarbons in sediments. In addition, organic matter and contaminants relating to organic matter are likely to become fixed in areas of fine sediment accumulation and when low energy conditions of hydrodynamic processes are present. Station 2 showed a negative correlation with TOCs and TPHs, which could imply that the local environmental or sedimentary processes (i.e, more current activity, less clay) would result in less sedimentary hydrocarbons being retained in the sediment, even if organic matter was present.. Another plausible explanation is that the organic matter in this station is primarily of natural origin (e.g., derived from terrestrial or marine productivity rather than being associated with petroleum pollution sources.

Overall, the predominance of positive correlations in the study area supports the notion that organic carbon plays a significant role in controlling the distribution and accumulation of petroleum hydrocarbons in surface sediments. The differences in relation between stations indicate that not only is the amount of hydrocarbons in sediments dependent on organic matter concentration at all stations, but that the concentration of hydrocarbons in sediments may also depend on some combination of hydrodynamic regimes, grain size distribution, and the level of pre-existing environmental contamination. Most studies report a positive TPHs-TOC relationship, suggesting that organic-rich sediments accumulate

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more hydrocarbons.

Tables 3 and 4 show the comparison of our results and the previous studies results

Researcher Study	Area	TOC%
Al-Saad et al., 2015	Basrah city	0.61-0.85
Hussian, 2015	Basrah city	0.48-0.8
Karem, 2016	West Qurna	0.762-2.187
Jaafar et al., 2019	Basrah city	0.57-4.05
Kadhim 2019	West Qurna-1	16-18.3
Jalal 2020	Basrah city	0.24-2
Salem 2022	Basrah city	9.9-20.5
Resen, 2024	Selected oil fields	0.42-26.63
Current study	Khor Al-Zubair	0.058-0.193

Figure 6. Table 3: Total Organic Carbon values comparison between the current study and previous studies.

Researcher name	Study area	TPHs concentration
Al-Hassen (2011)	**Basrah City**	8.33-16.83
Douabul et al. (2012)	**Basrah City**	13-38.8
Al-Ali et al. (2016)	**Basrah City**	2.2-75.05
Karem (2016)	**West Qurna-2 Oil Field**	16.657-37.372
Kadhim (2019)	**West Qurna-1 Oil Field**	9.52-31.04
Al-Halfy et al. (2021)	**Rumaila Oil Field**	0.5-93.95
Salem (2022)	**Basrah City**	4.95-685.19
Resen et al. (2024)	**Selected oil fields**	8.22-389.70
Current Study	**Khor Al-Zubair**	0.076-12.1586

Figure 7. Table 3: Total Organic Carbon values comparison between the current study and previous studies.

Conclusions

The present study demonstrated clear spatial and vertical variations in both total organic carbon and total hydrocarbon concentrations within the sediments of Khor Al-Zubair. The highest TOC and TPH levels were recorded in Station 5, suggesting stronger anthropogenic input and greater organic matter accumulation capacity in that area. Similarly, Station 3 had the lowest concentrations, suggesting that this station may have had a most likely relatively lower contamination level. The association between TOC and TPHs supports the role of organic matter in adsorption and retention of hydrocarbons, but more factors may have influenced distributions of each of the sampling stations, including sediment texture and degradation processes (natural or otherwise). Overall, findings presented here support the idea that in general, hydrocarbons are locally polluted in Khor Al-Zubair and not homogeneously distributed as a result of both natural sedimentary environment and anthropogenic specific impacts. The authors suggest that continuous hydrocarbon contamination monitoring should be made to understand historical pollution sources, as well as long-term measure to reduce impacts to the marine receiving environment.

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