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N-alkanes Sources and Distribution in the Sediment of Khor-Al Zubair Southern Iraq

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Abstract - In this study, sediment samples from five stations were collected, aliphatic compounds were extracted, and the samples were analyzed by using a gas chromatograph in order to determine the pollution levels caused by normal alkanes concentrations in the Khor Al-Zubair in Basrah. The highest concentration was 10.10965 ng/g in the fifth station, while the lowest concentration was 0.91264 ng/g in the third station. The results showed that anthropogenic was the dominant origin,where Carbon Preference Index (CPI) ranged from 0.7181 in the third station to 1.0592 in the fifth station, and Pristine/Phytane ranged from 0.316547 in first station to about 0.730581 in second station. The C17/Pristine ratio shows that the most common origin is the anthropogenic where it ranged between 0.773271 in the third station and 1.905842 in the fourth station, and C18/Phytane ranged from 0.974346 in the fourth station to about 2.770045 in the first station. The concentrations of total organic carbon (TOC) were determined in sediment samples. The highest concentration was 0.193 in the second station and the lowest concentration was 0.076 in the first station. According to our knowledge this study is the first to determine the n-alkane in Khor Al-Zubair region.

مصدر و توزيع الالكانات الطبيعية في رواسب منطقة خور الزبير , جنوب العراق

فاطمة فاخر أبو تراب [1] و عباس حميد محمد [1] و حامد طالب السعد[2]
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المستخلص - في هذه الدراسة تم حساب تراكيز الالكانات الطبيعية في منطقة خور الزبير في محافظة البصرة من خلال جمع نماذج الرواسب من خمس محطات واستخلاص المركبات الاليفاتية منها وحللت العينات باستخدام جهاز كروماتوغرافيا الغاز لتحديد نسب التلوث بالالكانات الطبيعية في منطقة خور الزبير . لقد تم تحديد أعلى تركيز في المحطة الخامسة حيث بلغت قيمته حوالي 10.10965 ng / g وأقل تركيز في المحطة الثالثة حيث بلغ 0.91264 ng/g من خلال النتائج وجد ان معظم المركبات المتواجدة في منطقة الدراسة ذات اصل غير طبيعي Anthropogenic حيث كانت نسب CPI تتراوح من 0.7181في المحطة الثالثة الى حوالي 1.0592 في المحطة الخامسة, اما نسبة Pri/Phy فقد تراوحت من 0.316547 في المحطة الأولى الى حوالي 0.730581 في المحطة الثانية و كانت نسبة C17/Pri في المحطة الثالثة حوالي 0.773271 حتى تصل الى 1.905842 في المحطة الرابعة و نسبة C18/Phy كانت حوالي 0.974346 في المحطة الرابعة بينما اعلى نسبة كانت في المحطة الأولى و التي بلغت 2.770045 . كذلك تم حساب اجمالي الكربون العضوي الموجود في الرواسب حيث بلغت اعلى قيمه له 0.193 في المحطة الثانية و اقل قيمة كانت في المحطة الاولى بلغت حوالي 0.076 . حسب علمنا فان هذه الدراسة الأولى التي تحدد الالكانات الطبيعية في منطقة خور الزبير.

الكلمات مفتاحية: البصرة, N-alkanes, خور الزبير , التلوث, TOC , CPI

Introduction

Hydrocarbons pollution is a serious environmental problem that has attracted significant attention from around the world. (Lompré *et al.*, 2018).
In aquatic environments, sediments provide valuable insights into the dynamics of substances such as chemical pollutants. (Al-Saad *et al.* 2020) .

Petroleum pollution has emerged as a major environmental concern due to the toxic components present in petroleum that can induce mutagenic and carcinogenic effects in living organisms. The primary factors contributing to the disposal of petroleum into the environment include the increasing global demand for fuel and the occurrence of accidental oil spills. (Al-Saad *et al.* 2015).

Normal alkanes are commonly found in costal water, the estuarine, as well as in the associated sediments (Lu *et al.*, 2023). N-alkanes are organic compounds that are stable, non-polar, and rarely reactive. They are also known as paraffins, which translates to "with a scarce chemical affinity" in Latin (Giuffrè, 2016).

Environmental dust, runoff, spills, sewage and industrial effluents, natural oil leakage and shipping operations are some of the anthropogenic and natural (bacteria, fauna and flora) sources of n-alkanes that enter the aquatic environment (Appolinario *et al.*, 2020).

Human activity and industrial development increased, there were more old oil wells, refineries, towns, and cities, which led to a rise in onshore oil use and accidents. Consequently, spills and storage losses have significantly increased, contaminating the rivers, estuaries, and shallow waters that are the focus of much research on oil pollution. Despite the lack of appropriate ports or depots for dependable transportation, marine development has grown quickly globally in recent years, leading to ecological and pollution issues in shallow seas and bays. (Lompré *et al.*, 2018).

Normal alkanes originate from various sources, including both geochemical and biological processes. Some of these petroleum vehicles are transported into the water column, where they become adsorbed onto sediment surfaces and ultimately settle at the bottom. The study of normal alkanes is important, as they are instrumental in identifying the sources of oil pollution, whether anthropogenic or biological in origin (Aboul- Kassim and Simoneit,1995).

The utilization of n-alkanes as geochemical markers is a widely utilized method for evaluating water and sediment contamination resulting from gasoline, crude oil, industrial wastewater discharge and diesel leaks. (Zhang *et al.*, 2024).

The aim of this study to determine the source and distribution of N-alkanes in sediment of Khor Al-Zubair and determine the total organic carbon (TOC%) in these sediment areas.

Materials and Methods

Study area:

The Khor Al-Zubair area is an important part of the Iraqi marine waters located northwest the Arabian Gulf, and it has significant importance for the country, including economic activities, industries, fisheries, and oil transportation. (Lafta *et al.*, 2019).

The geological structure of the region mainly consists of Quaternary sediments, including clay, silt, and sand, which are associated with diverse geological formations. Within the Northern Arabian Gulf Region, Khor Al-Zubair stands as the largest and most significant lagoon. (Hazza and Jassim,2024)**.**

The area covered by water in Khor Al-Zubair Creek is approximately 60 Km2, and the depth of the navigational channel in Al-Zubair Creek ranges from 10 to 20 meters. Northern part of Al-

Zubair Creek consists of several shallow, irregular tidal lakes with a complex geometry resembling the shape of tree fronds. (Lafta *et al.*, 2019)**.**

The area is also an important drainage outlet for a network of rivers that includes the Tigris and Euphrates. Through the waterway of the Al-Zubair River, the Al-Zubair Creek, a large outlet for saline water, connects to the Shatt al-Arab estuary. This river faces the Umm Qasr port, the main maritime port leading to the Arabian Gulf, and is geographically located at the mouth of the Al-Zubair River network. Due to its easy access to the open sea, it has become the most vital aquatic habitat for aquatic life that relies on the exchange of freshwater from the land and ready saline water in both seasons. This river is fed not only by the Al-Zubair River but also by other tributaries. There are few attempts to interpret the deposits of the Al-Zubair Creek and the surrounding area (Hazza and Jassim, 2024)(Figure 1)**.**

Samples were taken at five stations, each located roughly five kilometers apart throughout the study area. The samples were taken from the shallow area about 0-5 cm (Figure 2).

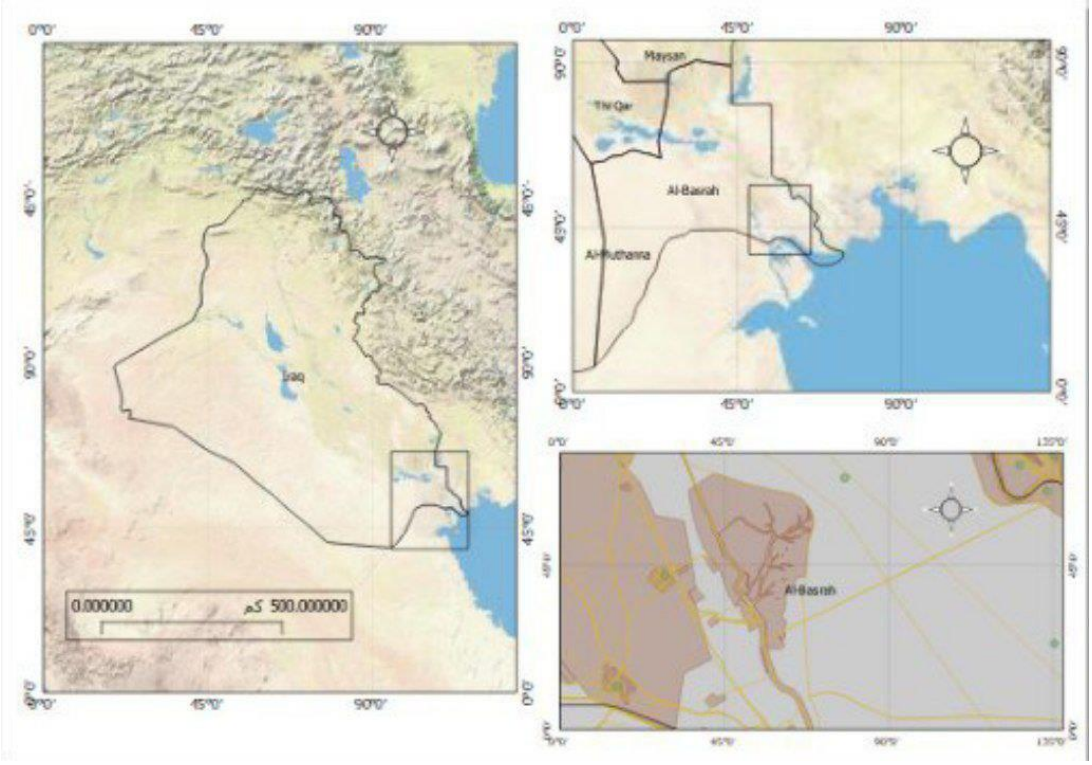

Figure 1. Study Area, Basra Southern Iraq.

Figure 2. Stations of sampling (Google Earth)

N-alkanes Analysis:

The samples were collected using a sampling core at depths at 0-5 cm. The samples were left until they dry naturally. Then samples were grounded using an electric grinder, and passed through a 63-micron sieve.50g of each sample is weighted, and adding about 0.5 g or less of copper, and 150 ml of a solvent made of a 3:1 mixture of methanol and methyl chloride, the sample is left in a KS500 LH fermentation incubator shaker for 24 h 150 rpm. After that the samples were filtered through filter paper, and allowed to evaporate the solvent. Following drying, the sample is eluted using glass wool, 5 g of silica gel, 1 g of anhydrous sodium sulfate and 1 g of aluminum oxide in a glass column. To separate the aliphatic compounds of the sample, 25 g of n-hexane is added. Then the sample is processed using gas chromatography (GC) (model 7890A, Agilent/USA), (the work done in Nahran Bin Umer Lab) (Goutx and Saliot, 1980; Al-Hejuje, 2014).

Total organic carbon (TOC):

The loss-on-ignition (LOI) method is an authoritative technique for determining organic matter. It decisively heats and destroys all organic components in soil or sediment, ensuring precise measurement and providing critical insights into the material's composition.

To prepare the samples for the analysis of total organic carbon (TOC%) using the combustion method described by Ball, the samples were grounded and then sieved through a 63-micron sieve to ensure uniform particle size. A crucible was dried and weighed, after which exactly two grams of the sieved sediment were measured and placed inside. The crucible was then placed into combustion at 550°C for two hours. Following combustion, the crucible containing sediment samples were moved to a desiccator to cool it and reach equipoise with the surrounding environment. It was then weighed multiple times until a constant weight was achieved. The total organic carbon (TOC) content was determined by calculating the weight difference before combustion and after combustion. (Ball,1964).

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

Where W1 is the weight of an empty eyelid, W2 is the weight of eyelid and sample weight of 1g before burning and W3 is the weight of eyelid with sample after burning.

Results and Discussion

About 34compounds, ranging from n-C8 to n-C40, were recorded. The total quantity and kind of normal alkanes found at each station are displayed in (Table 1) and their GC chromatograms show in (Figure 3).

Table 1. Concentration of N-alkane in sampling stations.

Component Name	Station 1	Station 2	Station 3	Station 4	station 5
n-C8	0	0	0	0	0
n-C9	0	0	0	0	0
n-C10	0	0	0	0	0
n-C11	0	0	0	0	0
n-C12	0	0	0	0	0
n-C13	0	0	0	0	0.01693
n-C14	0.012961	0.029253	0.02721	0.18218	0.23882
n-C15	0.010744	0.04792	0.01243	0.22395	0.2196
n-C16	0.169994	0.194634	0.10711	0.73277	0.51999
n-C17	0.021357	0.048384	0.02135	0.40846	0.292
Pr	0.019894	0.058925	0.02761	0.21432	0.19445
n-C18	0.174089	0.142491	0.09242	0.48766	0.51942
Ph	0.062847	0.080655	0.04023	0.5005	0.46669
n-C19	0.081287	0.049563	0.02944	0.23807	0.25838
n-C20	0.158797	0.112964	0.06733	0.41037	0.46577
n-C21	0.046359	0.029477	0.01196	0.20354	0.21066
n-C22	0.128241	0.07292	0.03928	0.26028	0.363
n-C23	0.07058	0.045004	0.01727	0.29072	0.29321
n-C24	0.068896	0.041857	0.01987	0.21205	0.23358
n-C25	0.13748	0.094446	0.02922	0.47562	0.58426
n-C26	0.125495	0.035716	0.01636	0.21152	0.3606
n-C27	0.23539	0.117816	0.05277	0.57032	0.70603
n-C28	0.155676	0.100451	0.02857	0.6259	0.76402
n-C29	0.137406	0.1453	0.0433	0.61992	0.73947
n-C30	0.070848	0.074803	0.01547	0.43716	0.52833
n-C31	0.052379	0.070401	0.07968	0.52785	0.59083
n-C32	0.049222	0.027266	0.00969	0.36694	0.45038
n-C33	0.055424	0.009124	0.04437	0.354	0.47394
n-C34	0.056249	0.007682	0.03687	0.18298	0.24619
n-C35	0.053196	0	0	0.04685	0.33197
n-C36	0.016699	0.02113	0.04283	0.011	0.01281
n-C37	0.023038	0	0	0.00627	0.02832
n-C38	0.015	0	0	0	0
n-C39	0	0	0	0	0
n-C40	0	0	0	0	0
TOTAL	2.209548	1.658182	0.91264	8.8012	10.10965

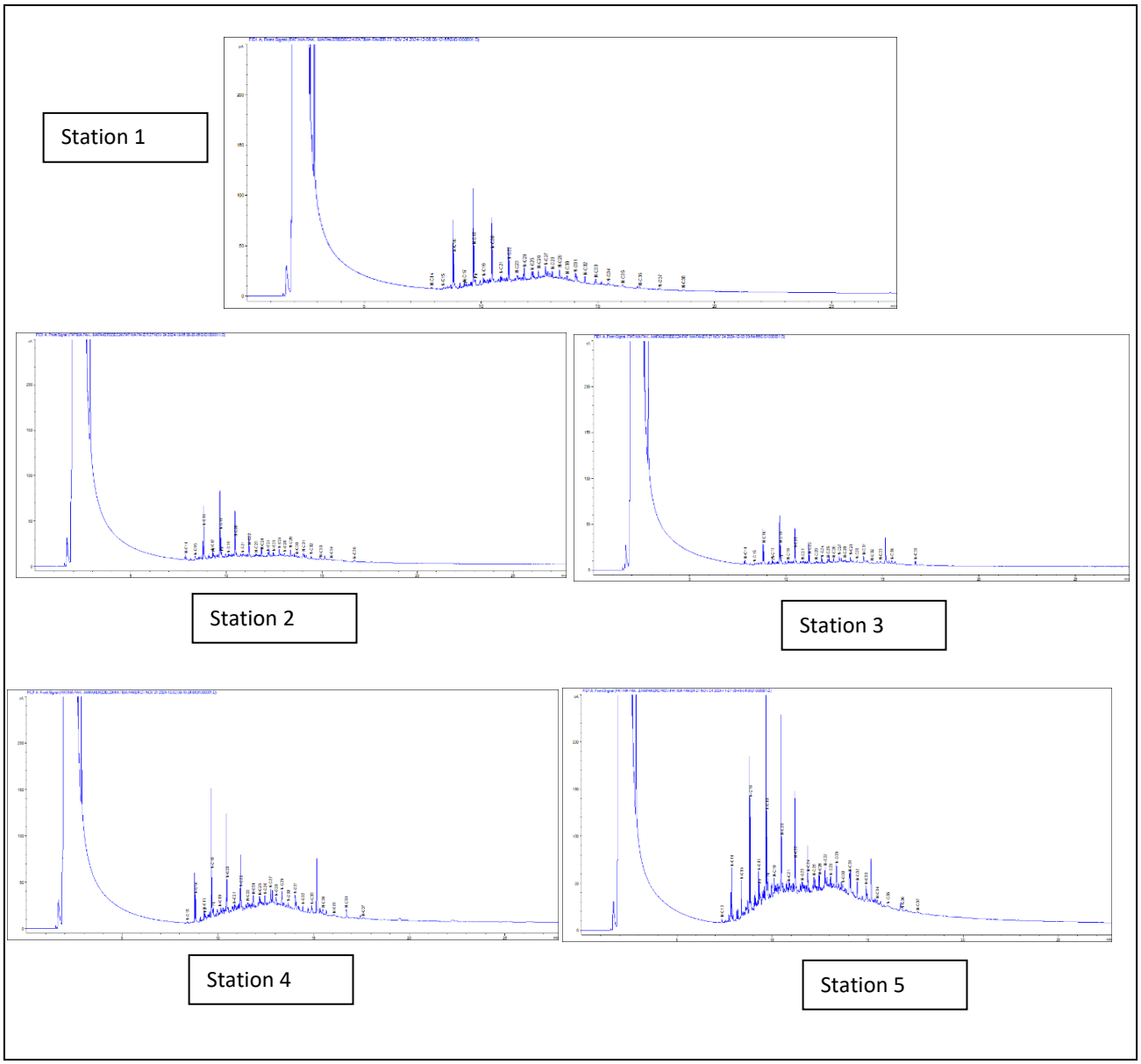

Figure 3. Chromatograms of sediment samples of the study stations.

N-alkanes, common in marine sediments, have a length of nC14 to nC34, are source-specific, and are resistant to degradation, which makes them useful biomarkers (Zhao *et al.*, 2022). The n-alkanes are synthesized by aquatic macrophytes, algae, terrestrial plants, and other microorganisms and bacteria. Normal alkanes in marine sediments are derived from the local sources, such as algae, terrestrial plants, as well as from unnormal inputs from bacteria. Distinct compositional patterns exist among the different sources: medium to short-chain n-alkanes (nC12 to nC22, particularly nC16 and nC18) originate from bacteria; marine algae produce medium to short-chain individual natural alkanes (nC13 to nC21, especially nC15, nC17, and nC19); medium-chain individual natural alkanes (primarily nC23 and nC25) are derived from algae. (Yang *et al.*, 2024); and long-chain normal alkanes (nC25 to nC34, with a dominance of nC27, nC29, and nC31) mainly comefrom merrestrial higher plants (Wang *et al.*, 2021).The origin of

the compounds found at each station was ascertained using a set of ratios included CPI, Pri/Phy, C17/Pri and C18/Phy.

These ratios are considered important indicators for clarifying the distribution, sources and composition of n-alkanes within sedimentary environments. (Zhao *et al.*, 2018). Normal alkanes resulting from anthropogenic sources exhibit (CPI) values of approximately 1 or less, whereas those derived from biogenic sources typically when (CPI) values more than 1. (Fagbote and Olanipekun, 2013). The ratio of pristane to phytane of more than one indicates a biogenic origin. Conversely, one or fewer points to pollution from petroleum hydrocarbons or anthropogenic sources. (Mzoughi and Chouba, 2011). Ratio of C-17 to pristane and C-18 to phytane if the percentage is less than one, it indicates the origin of oil and hydrocarbon weathering. Conversely, a high ratio indicates the presence of oil compounds. (Harji *et al.*, 2008).

This study suggests that the high molecular weight n-alkanes (HMW) were more ample than the low molecular weight n-alkanes (LMW). According to Al-Hejueje *et al.* (2016), this contradiction arises from the fact that LMW n-alkanes, particularly those ranging from C9 to C16, have the ability to evaporate and microbial degradation. In contrast, HMW n-alkanes, such as C28 to C31, exhibit greater resistance to biodegradation**.**

In this study the n-alkane in the samples ranged from C8 to C40. The dominant carbon numbers identified within the study areas ranged from C14 to C37. Normal alkanes with even numbers within the C12 to C24 range are primarily associated with contributions from microbial activity and petroleum sources. In contrast, the prevalence of natural alkanes with odd numbers within the C15 to C33 range, particularly C23, C25, C27, C29, and C31, indicates a biogenic origin, specifically from terrestrial plants. as reported by (Farid, 2017) **.**

The activities of extracting and producing oil fields have contributed to the increase in levels of n-alkanes (Li *et al.*, 2020). In aquatic environments, phytoplankton and algae serve as a source of carbon compounds with odd numbers, such as C15, C17, and C19 (Zhan et al., 2022). Otherwise, the presence of specific individual alkanes, including C25, C27, C29, and C31, has been used as an indicator to trace organic materials derived from terrestrial plants (Thomas *et al.*, 2021)**.**

Furthermore, (Chen *et al.*, 2021) suggest that typical even-carbon n-alkanes main source is diatoms. In contrast, the presence of C22 and C24 has been attributed to bacterial activity (Al-Bidhani *et al.*, 2020; Chen *et al*., 2021)**.**

N-alkanes with low molecular weight (C9-C15) can evaporate and decompose by microorganisms. However, the high molecular weight n-alkanes (C33-C36) are more resistant to biological degradation and stabilize in sediments and water. This explains the undetectable levels of C10-C15 and the low concentrations of C16-C17. Furthermore, while phytane is typically found in oil, pristane is usually associated with zooplankton (Guerra-García *et al.*, 2003)**.**

At the first station total compound concentrations had the highest percentage about (o.155676 ng/g) for n-C28 and the lowest at about (0.0107 ng/g) for n-C15. The lowest concentration at the second station was (0.00768 ng/g) for n-C34, while the highest concentration was (0.19463 ng/g) for n-C16. At the third station, the highest concentrations for n-C16, reaching (0.10711 ng/g), while the lowest concentration was for n-C32, reaching (0.00969 ng/g). At the fourth station, the compounds' lowest concentration was for n-C37, where it was approximately (0.00627 ng/g), and their highest concentration was for n-C16, where it was approximately (0.73277ng/g). The fifth station showed the lowest concentration (0.01281 ng/g) for n-C36 and the highest concentration (0.76402 ng/g) for n-C28 **.**

The highest total concentration at fifth station was (10.10965 ng/g) when the lowest total concentration was (0.91264 ng/g) in the third station.

The calculated ratios suggest that anthropogenic source were the dominant origin in the five stations. Where CPI ranged from 0.7181 in station 3 to 1.0592 in station 5, and Pri/Phy ranged from 0.316547 in first station to about 0.730581 in second station. The C17/Pri ratio show that the most common origin is the anthropogenic where it ranged between 0.773271 in the third station and 1.905842 in the fourth station, and C18/Phy ranged from 0.974346 in the fourth station to about 2.770045 in the first station. (Table 2).

Table 2. The ratio that was adopted to determine pollution.

	Station 1	Station 2	Station 3	Station 4	Station 5
Total	2.209548	1.658182	0.91264	8.8012	10.10965
Pri/Phy	0.316547	0.730581	0.686304	0.428212	0.416658
C17/Pri	1.07354	0.821112	0.773271	1.905842	1.501671
C18/Phy	2.770045	1.766673	2.297291	0.974346	1.112987
CPI	0.7775	0.7906	0.7181	1.0068	1.0592

We can see from the Pri/Phy ratio's results that the origin was anthropogenic, and the CPI shows that anthropogenic origin in first, second and third stations but it shows a biogenic origin in the fourth and fifth station **.**

C17/Pri results indicate that the compounds are of an oil weathering origin in second and third station, when it indicate to oil compounds in the first, fourth and fifth stations **.**

While the C18/Phy indicates that most compounds are of an oil compounds origin except station four are oil weathering origin**.**

Organic carbon consistently enters the sediment as a result of the decomposition of plant and animal remains, root secretions, living and dead microorganisms**.**

Figure (4) and table (3) present the TOC% concentrations in soil samples from the chosen stations. They indicate that the second station had the highest concentrations, approximately 0.193, while the first station had the lowest concentrations, approximately 0.076.

Table 3. Total Organic Carbon in sediment of study area.

TOC %				
Station 1	Station 2	Station 3	Station 4	Station 5
0.076	0.193	0.156	0.149	0.166

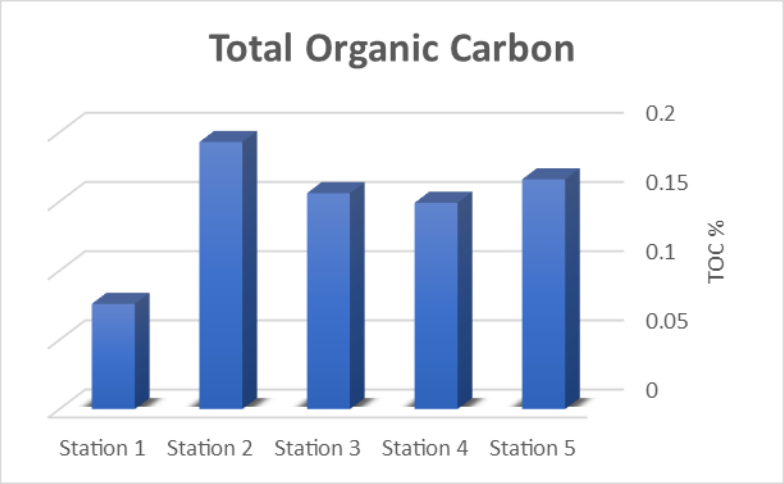

Figure 4. Total Organic Carbon Concentration.

Table 4 compares the concentrations found in this study with those found in other studies, and we find that the results in the range of previous studies.

Table 4. Comparison of previous studies with the current study.

Researcher name	Study area	N- alkane (µg g-1dw)
Douabul *et al*., (2012)	Basra City	9.2 - 42.9
(AL-Saad *et al*., 2015)	Basra City	3.575 - 21.266
Karem (2016)	West Qurna-2 Oil Field	5.392 - 24.240
Kadhim (2019	West Qurna-1 Oil Field	5.868 - 17.788
Al-Halfy *et al*., 2021	Rumaila Oil Field	99.99 - 100
Saleem (2022).	Basra City	10.317 – 410.812
Resen *et.al.* 2024	selected station in Basra oil field	112.169-651.333
Current study	Khor Al-Zubair	0.91264-10.10965

Conclusions:

The results of this study will be used as a guide for future research as it is the first to focus on studying the levels of aliphatic compounds in the Khor Al-Zubair area. We found approximately 34 components of n-alkanes from n-C8 to n-C40, with total concentrations in the sediments ranging from 0.91264 nanograms/gram at the third station to 10.10965 nanograms/gram. It was found that most of the compounds present in the study area are of anthropogenic or hydrocarbon origin, indicating significant pollution in the area.

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