Evaluation the Distribution and Sources of n-Alkanes in Sediments of the Tigris River at Amara City, Iraq

Muayad H.M. ALbehadili[1]., Ali H. Amteghy[1]., Salah M. Saleh[1], Fadal, J. Farhan[1] .,Maha K.AL-Mishrey[2] and Hamid T. AL-saad[1, *]

[1] College of Marine Science, University of Basrah, Iraq.

[2] Department of Biology, College of Science, University of Basrah, Iraq

[1*]Marine Science Center, College of Marine Science, University of Basrah, Iraq.

Abstract: -

This study investigates the distribution, sources, and environmental implications of n-alkanes in surface sediments from five stations along the Tigris River in Amara City, Iraq. Sediment samples were analyzed by using GC/FID for n-alkanes concentrations (C14–C36), total hydrocarbons, Carbon Preference Index (CPI), and diagnostic ratios (e.g., Pristane/Phytane, C17/Pristane, C18/Phytane). Results revealed significant spatial variability, with total n-alkane concentrations ranging from 0.99 µg/g (Station 4) to70.96 µg/g (Station 1). High CPI values (16.71 at Station 5) indicated the dominance of terrestrial plant inputs, while lower CPI values (1.11 at Station 1). Besides, the C17/pristane these referred to weathering of oil and hydrocarbons, while the C18/phytane indicates the presence of oil hydrocarbons at Station 3. However, at Station 4, the C17/pristane and C18/phytane referred to the presence of oil hydrocarbons. Urgent measures to control petroleum spills and long-term monitoring are recommended to mitigate ecological risks.

Keyword: N-alkanes, Sediment, Tigris River, Amara city, GC/FID

Introduction

municipal sewage, petroleum processing waste, and agricultural runoff contributes a complex mix of hydrocarbons to the sediment (Al-Sekar & Al-Dabbas, 2022) (Abdullah et al., 2018; Al-Mahmood et al., 2021). These contaminants pose serious risks to both aquatic ecosystems and public health. However, detailed information on n-alkane distributions in sediments from this region is still limited. Earlier investigations have reported petroleum-related pollution in Basrah (AlMaarofi et al., 2012) (Al-Saad et al., 2012) highlighting the urgent need to identify and quantify organic pollutant sources in the Tigris River.

This research focuses on analyzing the distribution, concentration, and origins of n-alkanes in sediment samples from the Tigris River near Amara City. The study's objectives are to: (1) measure N-alkane homologs ranging from C_{14} to C_{36} to evaluate spatial patterns; (2) use molecular diagnostic ratios such as CPI, Pristane/Phytane (Pri/Phy), C_{17}/Pristane, and C_{18}/Phytane to distinguish between terrestrial, aquatic, and petroleum-based sources; and (3) link n-alkane compositions with human-induced activities in the region. The results will provide essential baseline data to support future pollution control strategies in Iraq's environmentally sensitive river systems.

N-Alkanes act as molecular indicators for identifying the origin of organic matter in aquatic environments. Their compositional features—such as a preference for odd- over even-numbered carbon chains—help differentiate between natural biological sources like vegetation and algae, and petrogenic inputs such as crude oil and urban runoff. Given the Tigris River's crucial role in supplying water for agriculture and consumption in Iraq, and its increasing exposure to contaminants from urban and industrial sources in Amara City, this study investigates the sedimentary n-alkane distribution to better understand pollution sources and guide management efforts.

Location of Study and Collection of Sample: -

Al-Mashrah River is a short natural river in Iraq, one of the branches, that branched from the left side of the great Tigris River. Al-Mashrah district was located at approximately 25 Kilometers away from the city center of the Amara governorate southern Iraq. Five stations where selected for sampling as shown in Fig(1) which are:

Station 1: - is located on the Tigris River, fifteen kilometers before entering the city of Amara.

Station 2: - is located on the Tigris River - Al-Mashrah River near the bridge in (Al-Majidiyah area), which is a densely populated area.

Station 3: - is located far outside the governorate and away from residential areas.

Station 4: - is located on the high slope of the Al-Mashrah River (outside the city of Amara) at a distance of twenty kilometers.

Station 5: - is located at Al-Mashrah, towards Al-Mashrah Marsh, at the end of Al-Mashrah district.

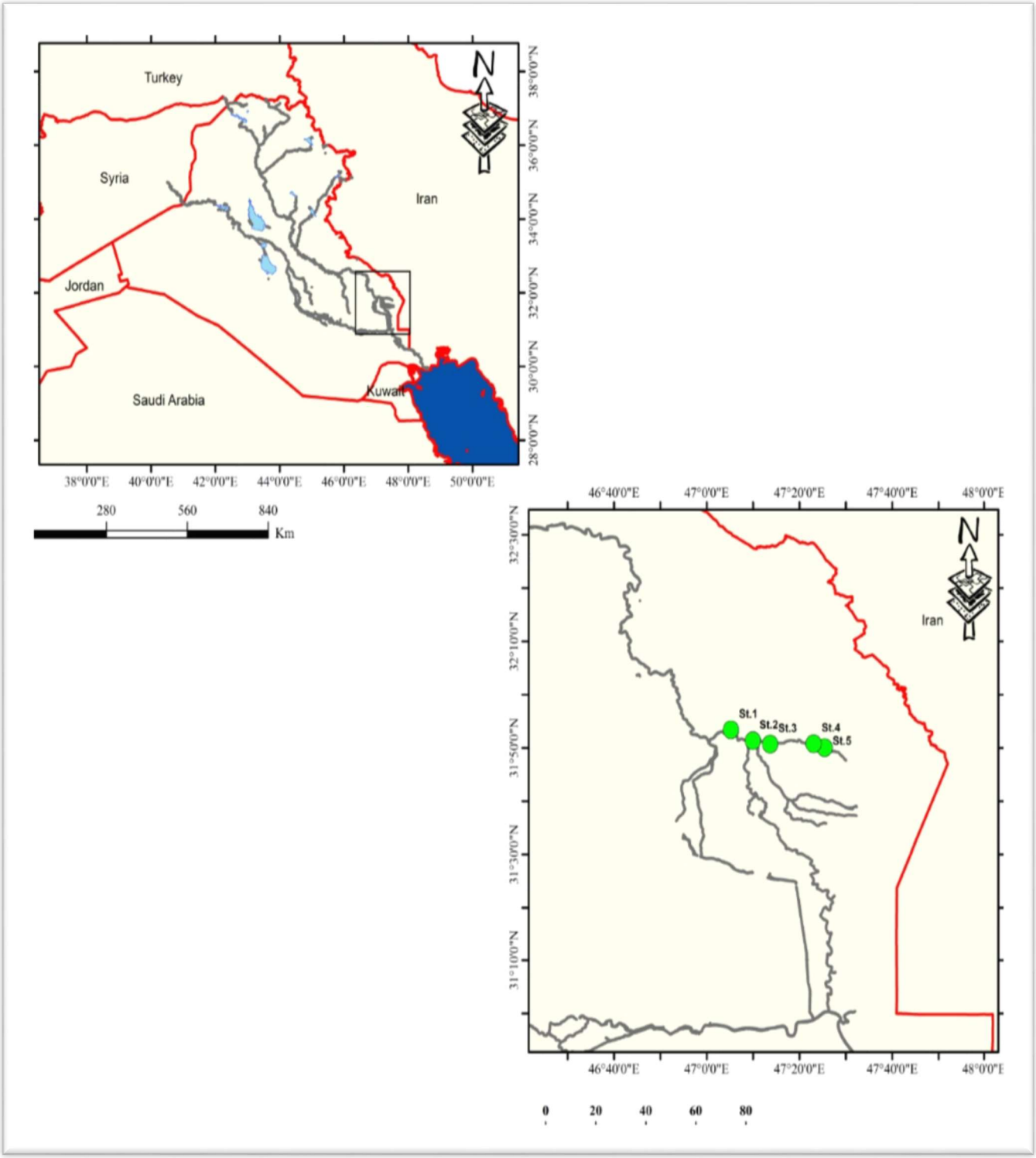

Figure (1) The Sample Locations

Materials and Methods: -

Sediment samples were oven-dried at 50 °C, finely ground using an electric mortar, and passed through a 63 µm mesh sieve. The processed samples were stored in glass containers until further analysis. For extraction, 50 grams of the sieved sediment were placed in cellulose thimbles and subjected to Soxhlet extraction following the procedure described by(Goutx & Saliot, 1980) and(Kadhim et al., 2019) . A solvent mixture of methanol and benzene (1:1, v/v; 120 mL total) was used for 48 hours, ensuring the temperature did not exceed 40 °C.

The combined extracts underwent saponification for two hours at the same temperature using 15 mL of 4 M potassium hydroxide (KOH) in methanol (MeOH), then cooled to room temperature. The non-saponifiable fraction was separated using 50 mL of n-hexane in a separatory funnel.

For fractionation, a 20 cm glass column was packed sequentially with glass wool, 8 g of silica gel (100–200 mesh), 4 g of aluminum oxide (Al_2O_3, 100–200 mesh), and topped with 4 g of anhydrous sodium sulfate (Na_2SO_4). The aliphatic hydrocarbons, including the n-alkanes, were isolated by eluting the column with hexane.

Gas chromatography (GC) was used To identify and quantify aliphatic compounds (C14-C36) in sediment samples, Helium served as the carrier gas in the liquid GC system, maintaining a linear velocity of 1 mL/min. A Flame Ionization Detector (FID) was used for detection, with operating temperatures of 280◦C for the injector and 300◦C for the detector. Separation of aliphatic compounds was achieved using an Agilent 19091J-101HP-5 column, which is a 5% phenyl methyl siloxane phase, with dimensions of 50 meters in length, 200 micrometers in internal diameter, and a 0.33 micrometer film thickness. The column temperature program started at 35◦C, held for 13 minutes, then increased at a rate of 5◦C/min until it reached 280◦C, where it was held for 60 minutes.

Results and Discussion: -

Table 1 presents the concentrations and distribution patterns of N-alkanes (C14–C36) across five monitoring stations in Amar City, located in the Messan Governorate. The total concentrations of aliphatic hydrocarbons varied significantly among the stations, ranging from 70.95 μg/g at Station 1 to 0.99 μg/g at Station 4, as illustrated in Figure 2. Table 1 also reveals a clear predominance of odd-numbered carbon chains—particularly C25, C27, C29, C31, and C35—at Station 1, and C27 and C29 at Station 2. Interestingly, C25 was the dominant compound at all five stations. This prevalence of long-chain odd-numbered n-alkanes is typically associated with terrestrial plant waxes(McInerney, 2013)alkanes (ranging from C15 to C21). In contrast, the low concentrations of short-chain n-alkanes, suggest limited contributions from aquatic or microbial sources and may also imply potential petroleum contamination (Yunlong Yu, 2016).Consequently, The detected n-alkane distribution patterns reflect contributions from both natural sources, such as vegetation and soils, and anthropogenic activities, including urbanization and industrial processes in Amar City. The dominance of plant-derived n-alkanes indicates substantial input from natural organic matter, whereas localized signatures of petroleum compounds point to human-induced influences.

The table (2) was explained the sources of aliphatic hydrocarbons at five stations at Messan governorate. There many factors were measured to determine the sources of hydrocarbons such as CPI, Pri/Phy, C17/C18, C17/PRI, and C18/Phy as mention in table (2).

Carbon Preference Index (CPI) gives an information about that source of the aliphatic hydrocarbons either biogenic or anthropogenic depending of the value of CPI, if the odd of hydrocarbons to even aliphatic hydrocarbons more than one referred the odd aliphatic hydrocarbons bigger than even aliphatic hydrocarbons, which resulted from decaying of wax of old plans (Ardenghi et al., 2024) .

Besides, the ratio of Pri/Phy was used as an indicator for determine the source of aliphatic hydrocarbon, where the pristine and phytane are two branch groups derivative from two straight chains heptadecane (n-C17) and octadecane (C18). Consequently, the ratio more than one that the source of hydrocarbon is biogenic, however if the ratio less than one the source of hydrocarbons is human anthropogenic.

Therefore, the stations three and four are biogenic sources of hydrocarbon Fig(4)but the station one, two, and five no detection of this parameter. Moreover, the C17/pristane and C18/phytane ratios are powerful tools that give clear insights into the geological history of hydrocarbons, making them necessary for determining the source of petroleum hydrocarbons. Table (2) was illustrated that at station three and station four, the C17/pristane less than one these referred to weathering of oil and hydrocarbons at station three, while C18/phytane more than one, it indicates presence of oil hydrocarbons. However, at station four, it indicates the presence of hydrocarbons for two indicators C17/pristane and C18/phytane because both then more than one N-alkanes(Al-Bidhani et al., 2021; Saleh et al., 2020; Shabar et al., 2025)

This study is conformed with many Studies (Table 3) from the Mesopotamian marshes and Lower Mesopotamia (Al-Hejuje, 2014) confirm that the dominant n-alkane signatures in sediments and soils are linked to these plant types, especially reeds, grasses, and riparian trees. Grasses are abundant in southern Iraq, especially in marshland and riparian environments.

Conclusions: -

The n-alkane distribution in Al-Amar City sediments indicates varied micro-environments. Stations 1, 2, and especially 5 show a strong influence from vascular plant inputs, suggesting they are near substantial marsh or land-based vegetation with little petroleum contamination. Station 5's exceptionally high CPI and C25 prevalence point to a distinct, localized plant source. Conversely, Stations 3 and 4 exhibit clear signs of petroleum pollution combined with biogenic contributions, mirroring the typical anthropogenic contamination found in studies of southern Iraqi aquatic systems. This diversity highlights the necessity of localized sampling to comprehend environmental conditions within a city or region.

Table (1) of Aliphatic Hydrocarbons in Five stations of Messan Governorate

Concentration	St_1	St_2	St_3	St_4	St_5
N-C14	0	0	0.4038175	0	0
N-C15	0	0	0	0	0
N-C16	0	0	0	0	0
N-C17	0	0	0.4405825	0.127788	0
N-C18	1.49952	0	2.0002725	0.1730755	0
N-C19	2.85451	0.84635	0.6657275	0.046785	0.5100125
N-C20	0.985865	0	0	0.04654725	0
N-C21	0.9651675	0	0.580095	0	0
N-C22	0	0	0	0	0
N-C23	0	0	0	0.11763975	0
N-C24	0.4629875	0	0	0	0
N-C25	9.5671225	0.9566275	0.7808775	0	18.66515
N-C26	6.726385	1.377615	0	0.0662045	0.59339
N-C27	0	5.6283125	0.5527225	0	0
N-C28	5.951025	1.799215	0	0	0.65985
N-C29	17.554485	3.87989	0	0.229417	0.746575
N-C30	9.0993725	0.7258625	0	0	0
N-C31	5.7778625	1.504075	1.2004	0.09821825	1.0154875
N-C32	6.6824725	0	0	0	0
N-C33	0.5728225	3.5655275	0	0	0
N-C34	0	0	0	0	0
N-C35	0	0	0	0	0
N-C36	2.25544	0	0	0	0
Total	70.9550375	20.283475	6.624495	0.989339	22.190465
Odd	37.29197	16.3807825	4.220405	0.619848	20.937225
Even	33.6630675	7.46822	2.40409	0.28582725	1.25324
Odd/Even	1.11	2.193	1.76	2.17	16.71
Pr	ND	ND	0.52687	0.04390375	ND
Phy	ND	ND	0.3016775	0.03976	ND
C17/Pri	ND	ND	0.836	2.912	ND
C18/Phy	ND	ND	6.631	4.353	ND

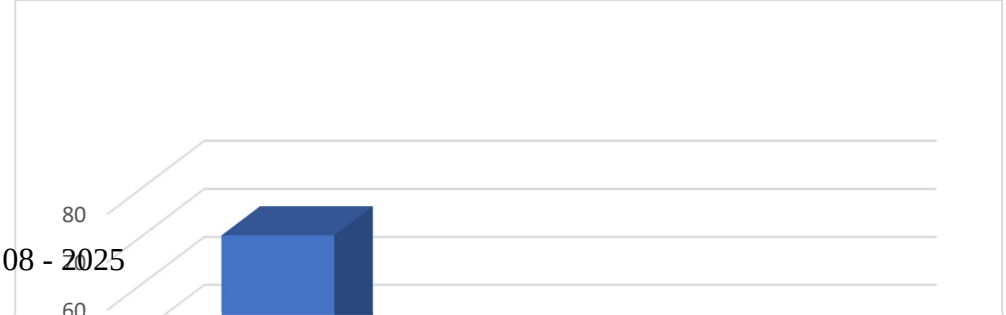

Table (2) N-Alkane's Source indices values in sediment at Five Station

Stations	CPI	Pri/Phy	C17/PRI	C18ta/Phy
St_1	Biogenic	ND	ND	ND
St_2	Biogenic	ND	ND	ND
St_3	Biogenic	Biogenic	0.836	2.912
St_4	Biogenic	Biogenic	6.631	4.353
St_5	Biogenic	ND	ND	ND

Table (3) Comparison with Other Studies

Study Location	Dominant n-Alkane Range	Source Indication	Reference	Notes
Amar City, South Iraq	C27–C33	Terrestrial plants	Current study	High odd-over-even predominance
Al – Hammar marsh,	C20–C31	Terrestrial plants, minor petroleum	(Al-Bidhani et al., 2021)	Riverine and urban influence
Tigris River, Iraq	C27–C33	Terrestrial plants	(Al-Hejuje, 2014)	Similar odd-carbon dominance

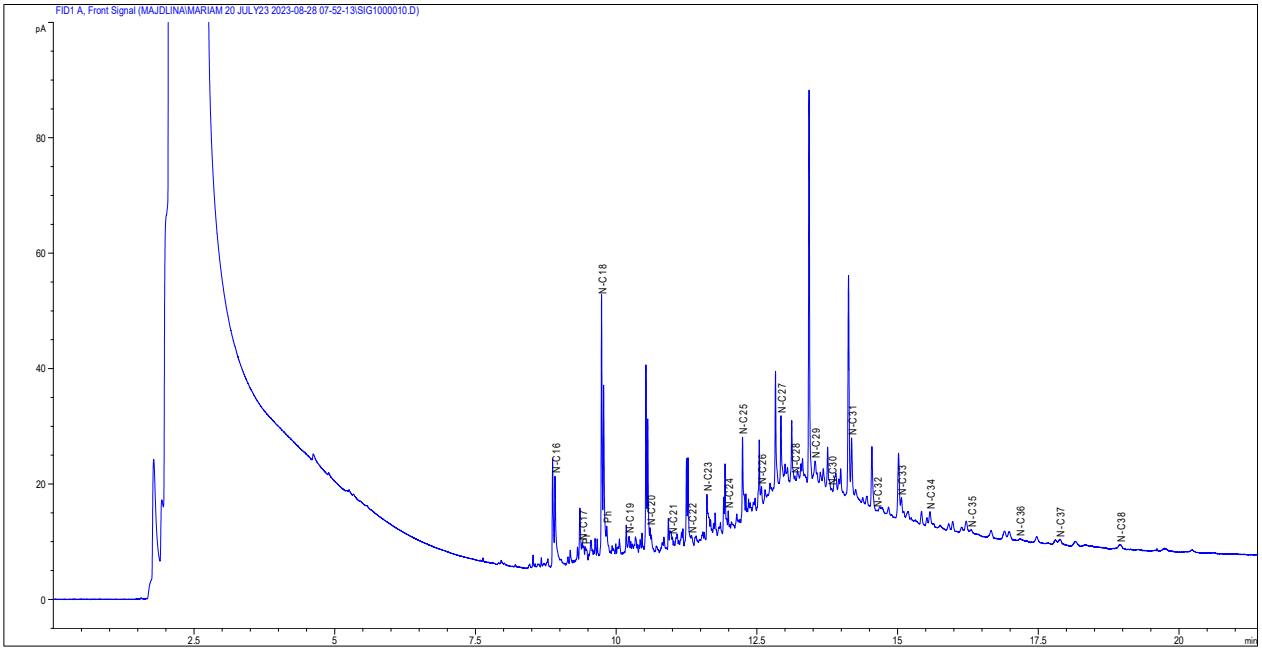

Fig (4) chromatograms of n-alkanes

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