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The origins and Sources of polycyclic Aromatic Hydrocarbons (PAHs) and Aliphatic Hydrocarbons (N-Alkanes) in The Tigris, Euphrates, and Shatt Al-Arab rivers

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Abstract. Samples were taken from three sites along the Tigris, Euphrates, and Shatt Al-Arab Rivers between November 2022 and July 2023 to ascertain the concentrations, distribution, and sources of PAH compounds and aliphatic hydrocarbons in water samples. Aliphatic (n-alkane) compounds' carbon chain lengths were measured from C7 to C38, and the total amount of n-alkanes in water varied between 48.09 µg/l and 276.98 µg/l. The heavy PAHs were fluoranthene and chrysene, whereas the light PAHs were carbazol and anthracene, with concentrations ranging from 45.16 to 1848.54 ng/l. The LMW/HMW, CPI, and Pristine/Phytoene ratios indicated that n-alkane hydrocarbons were primarily biogenic, pyrogenic, and at least petrogenic. Nonetheless, the LMW/HMW, Phenanthrene/Anthracene, and Flouranthene/Pyrene ratios showed that the primary sources of PAH molecules were petrogenic and pyrogenic environments.

Highlights:

1. Samples from Tigris, Euphrates, Shatt Al-Arab analyzed for PAHs, n-alkanes.
2. n-Alkanes (C7–C38) ranged 48.09–276.98 µg/l; PAHs 45.16–1848.54 ng/l.
3. Sources: biogenic, pyrogenic, petrogenic for n-alkanes; petrogenic, pyrogenic for PAHs.

Keywords: water, Tigris, Euphrates, N-alkanes, polycyclic aromatic hydrocarbons (PAHs), and Shatt Al-Arab

Introduction

The environment is at risk of pollution from petroleum hydrocarbon compounds, which can harm soil, surface water, and groundwater. This can lead to several environmental and health issues [1]. Moreover, removing these pollutants from the environment is a practical concern. Garbage from households and businesses, as well as from public transportation, oil tankers, oil exchanges, and electrical power plants, is a significant source of these pollutants [2]. Furthermore, the disposal of heavy industrial waste results in the infiltration of various contaminants into the water of the river [3].

It has been demonstrated that common water contaminants and hydrocarbon molecules negatively affect human and environmental health [4]. All aspects of the environment contain them, and they can bioaccumulate. The potent damaging effects of hydrocarbons [5].

Hydrocarbon molecules from petroleum are a significant cause of pollution in aquatic environments. The class of hydrocarbons known as N-alkanes, which have odd and even carbon numbers up to 64, lack an alkyl branch or replacement. Numerous processes, including recent benthic biosynthesis, decomposition, and geochemical reactions, as well as sinking chemicals from the water column, allow N-alkanes to enter the sediments of the aquatic environment [6].

Interest in PAHs has been high due to their ecological risk, economic impacts, and impact on human health [7]. Environmental contaminants that are carcinogenic, persistent, genotoxic, and toxic are referred to as PAHs [8].

Polycyclic hydrocarbons can be classified as either low molecular or high molecular. Because low molecular polycyclic hydrocarbons are soluble in water, volatile, and have two to three fused rings, they are vulnerable to degradation processes. More are polycyclic hydrocarbons with larger molecular weights. In contrast to four fused rings, they are less soluble, less volatile, and more lipophilic than low-molecular polycyclic hydrocarbons [9, 10]. PAHs may primarily originate from natural and man-made events (e.g., combustion processes, petrochemical industry effluents, volcanic activity, forest fires, and oil spills) [11].

The purpose of thisstudyis toidentifytheorigins andsourcesofpolycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (N alkanes) in the waters of the Euphrates, Tigris, and Shatt Al-Arab Rivers.

Methods

Water samples were taken from the Shatt Al-Arab River, the Tigris and Euphrates, and three sites (Table 1). The study was carried out from October 2022 to July 2023.

Table 1: The coordinates of the study station

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Stations	River	GPS Coordinates	
Station 1	Tigris	31.0608 N	47.4347 E
Station 2	Shatt Al-Arab	31.0037 N	47.4417 E
Station 3	Euphrates	30.9322 N	47.2937 E

Water samples from each of the three stations were collected using dark glass bottles at a depth of at least 20. Forty milliliters of chloroform were then used to keep them in place. The gathering of the samples was never impacted by rain. Hydrocarbons in a 5L water sample were extracted by mixing it minutes, per UNEP (1989).

Using an electric the remaining 1 liter was transferred to the separating funnel. Shuddered The separating funnel was left to separate the two levels after rigorous labor for fifteen minutes. After carefully passing the organic phase (lower layer) through a 100 mL glass container, the sample was obtained.

Helium is used as a carrier gas in liquid gas chromatography and has a linear velocity of 1 milliliter per minute with a flame ionization Detector (FID). The injector and detector had operating temperatures of 320°C and 320°C, respectively, for aliphatic separation. For two minutes, the column's initial temperature was kept at 40°C. After that,. "However, the column temperature was kept at 25°C as the initial temperature for one minute before rising by 3°C per minute to 320°C. The injector and detector operating temperatures for the PAHs separation were 320°C and 300°C, respectively.

Hydrocarbon pollution indices:

The source of hydrocarbons in aquatic settings was identified using the hydrocarbon contamination indices. The following is an illustration of these indices:

1- Evidence used to determine the origin of alkanes (n-alkanes), including: -

1 - LMW / HMW

While most mostly sourced from terrestrial vascular plants. The total aliphatic hydrocarbon concentrations from C7 to C26 add up to LMW, while from C27 to C40 add up to HMW. Natural inputs from terrestrial biological sources are indicated by a ratio less than one, those from biological sources by a ratio greater than one, and petroleum sources by values around one.

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2- Carbon Preference Index (CPI):

The total concentrations of alkanes with odd carbon numbers to the total concentrations of alkanes with even carbon numbers is its definition. The hydrocarbons come from a petroleum source when the CPI value is equal to 1, while pyrogenic and carbonate-derived oils are indicated when the CPI value is less than 1. or minerals that have evaporated (sources of combustion).) Alkanes in aquatic settings have a biological origin when their CPI value is more than 1 [12].

$$CPI= \sum Odd / \sum Even$$

3-Pristane/Phytane Ratio:

The sources of aliphatic hydrocarbons (n-alkane) in aquatic settings were identified using the ratio of pristane concentration to phytane concentration. The hydrocarbons are of petroleum origin if the ratio is equal to one; if it is greater than one, alkanes in aquatic settings have a biological origin. It comes from combustion processes if the ratio is less than one.

4- Unresolved Complex Mixture (UCM):

Generally regarded as a mixture of several structurally that are incapable of being separated by a capillary GC column, UCM manifests as a hump in the baseline chromatogram. They are a result of both the human contribution of hydrocarbon compounds to the environment and the presence of complex petroleum hydrocarbons [13].

2- The following evidence was used to identify the source of polycyclic aromatic hydrocarbons:

1 -The LMW/HMW ratio is the weight ratio of low to high molecular weights.

is greater than (1); if the ratio is less than (1), the source is incomplete fuel combustion. LMW is the total of the light polycyclic aromatic hydrocarbons (2–3 rings) concentrations. HMW is the total of the heavy polycyclic aromatic hydrocarbon concentrations (four rings and beyond).

2. The ratio of the anthracene to phenanthrene (phe. /anth).

If the percentage then the source of the PAHs is petroleum, and if the percentage is smaller than the number (1), then the source of the PAHs is from burning fuel

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3-The ratio of fluoranthene to pyrene (Fluo. /pyr.).

If the percentage and if the percentage is smaller than one (1), then the source of the PAHs is petroleum [14].

Result and Discussion

The results were displayed seasonally, with October and November representing the fall season, March and April spring season, June and July representing the summer. Symbolized the summertime.

Water containing N-alkanes:

Aliphatic chemical carbon chain lengths were determined in water samples C7 through C38. In the Tigris station, the paired carbon chains C18 and C26 were more common, whereas in the Shatt Al-Arab and Euphrates stations, the paired carbon chains C18 and C24 were more common. In Figure 1, the percentage of each alkane component in water is shown. Phytane and pristine are among the other hydrocarbons found in the aliphatic portion.

reported the lowest concentration of total aliphatic hydrocarbon compounds in water samples (48.09) in the summer, while the Tigris station recorded the highest quantity (276.98) micrograms/liter in the spring. Based on statistical analysis utilizing the ANOVA test one-way.

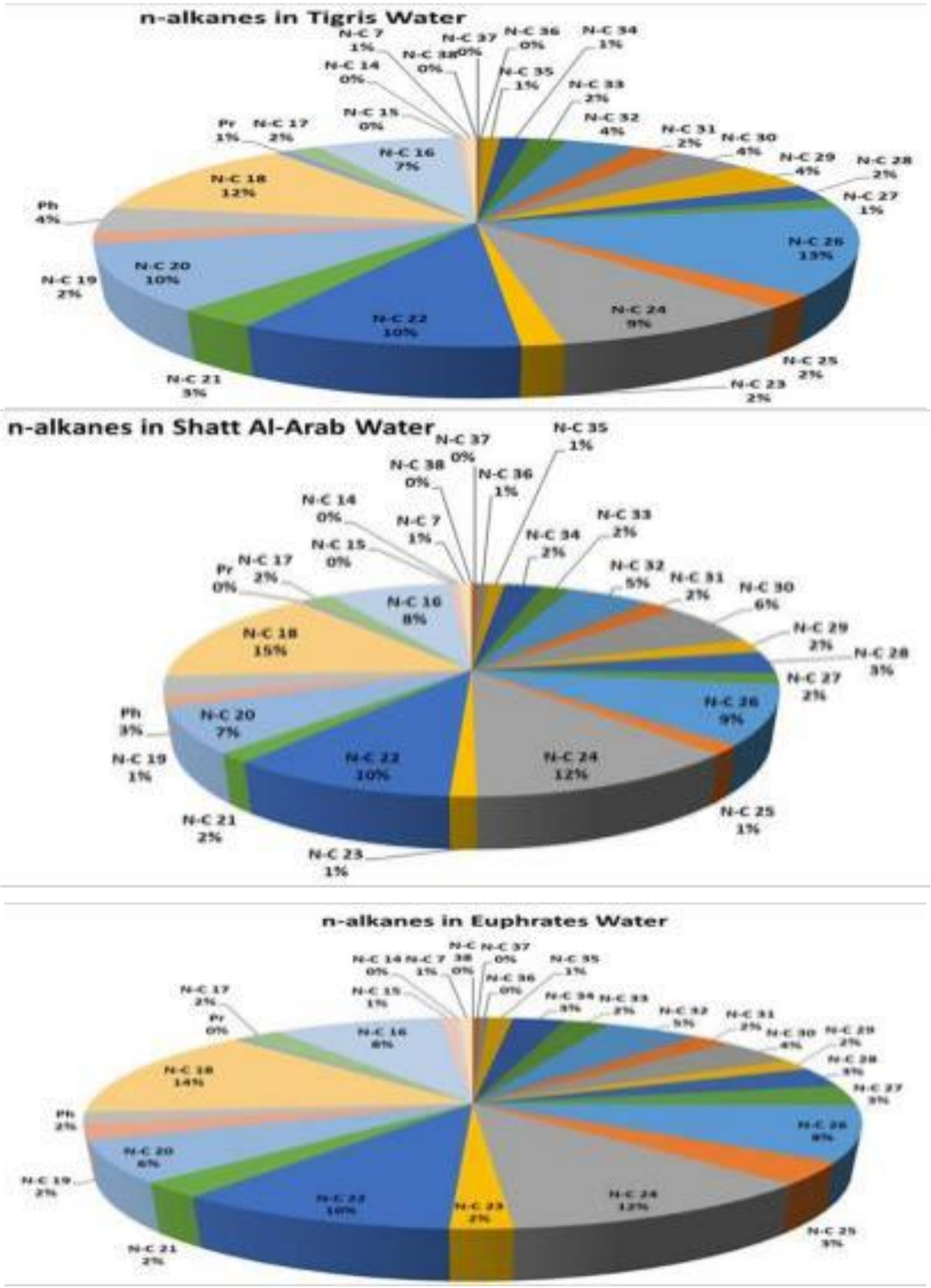

Figure 1 shows the proportions of aliphatic hydrocarbon (n-alkane) components in the study stations' water.

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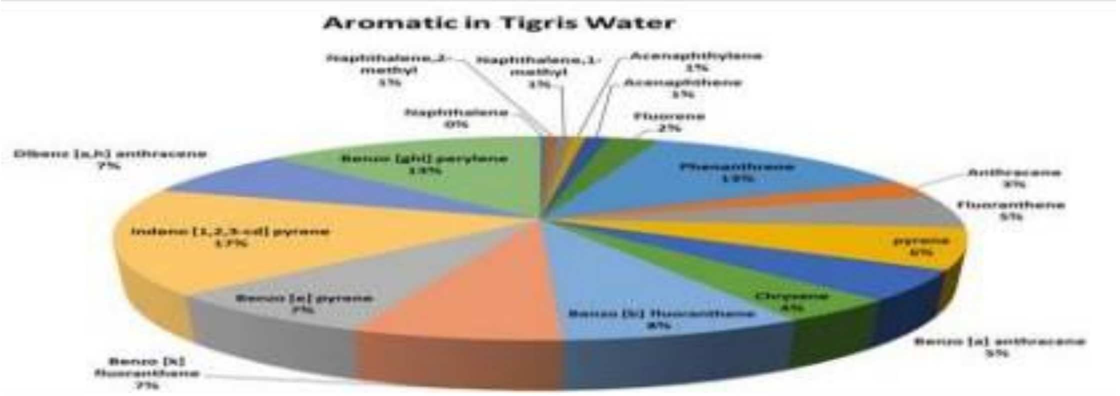
PAHs in water:

In the water in the Tigris and Shatt al-Arab stations, the primary aromatic hydrocarbon compounds, benzo[ghi]perylene, and phenanthrene; in the Euphrates station, the primary aromatic hydrocarbons are pyrene, benzo[ghi]perylene and phenanthrene. According to figure (2).

In the spring, the Tigris station recorded the highest concentration of total aromatic hydrocarbons (1848.54 ng/L) in water samples, whereas in the fall, the Euphrates station recorded the lowest concentration (45.16 ng/L). An analysis of variance (ANOVA-test one way) based on station-specific and seasonal data showed significant differences (p≤0.05).



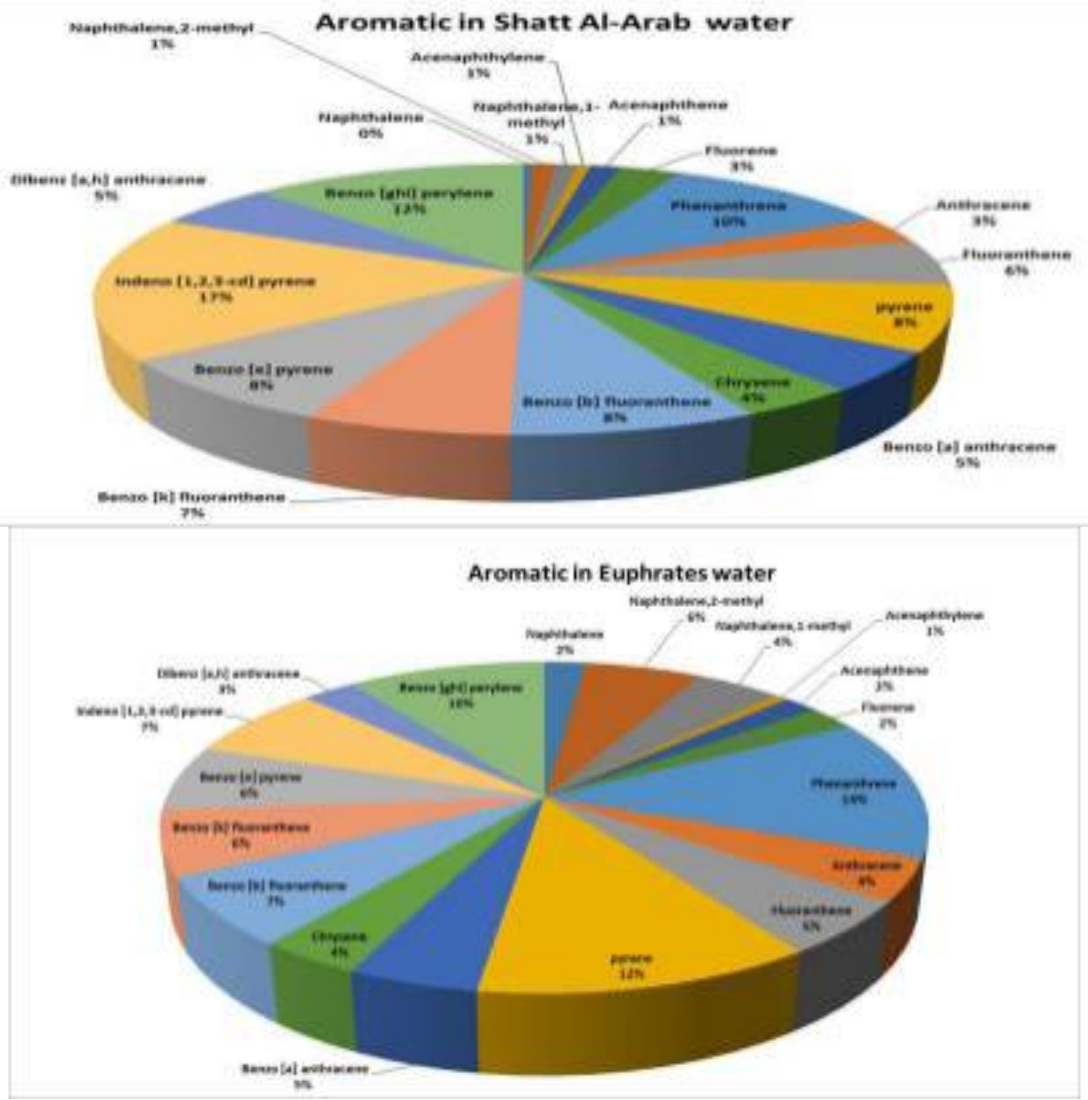


Figure 2 Percentages of aromatic hydrocarbon compounds for water samples at the study stations.

Indices of Hydrocarbon Pollution:

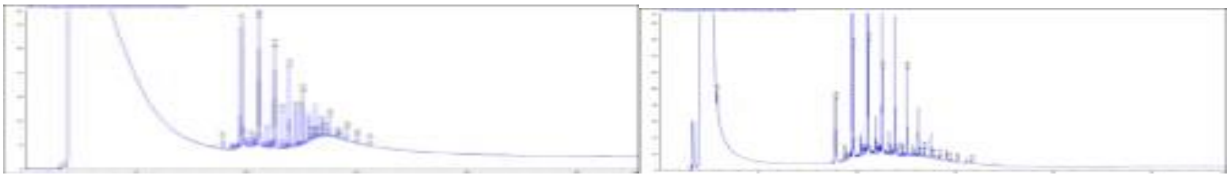
Pollution indicators for N-alkanes:

The CPI number and the LMW/HMW ratio both describe it. With most water samples having undetectable pristane and phytane values and only a few having both, the pristine/phytane ratio was harmful, as Table (2) demonstrates. A pyrogenic source of n-alkanes in the water samples was suggested by the overall values (for all stations during the study period) of the pristane/phytane ratio (0.09), which were less than one.

A little proportion of the water chromatograms in the baseline chromatograms showed UCM as a hump (Fig. 3).

Table (2) lists the amounts of evidence of aliphatic chemical pollution in water samples from the stations under analysis during the study period, along with a description of the compounds' original source.

Stations	Seasons	LMW/HMW	Descriptions	CPI	Descriptions
Station 1	Autumn	2.17	Biogenic	0.26	Pyrogenic
	Winter	2.98	Biogenic	0.17	Pyrogenic
	Spring	5.29	Biogenic	0.45	Pyrogenic
	Summer	1.64	Petrogenic	0.28	Pyrogenic
Station 2	Autumn	2.07	Biogenic	0.25	Pyrogenic
	Winter	3.23	Biogenic	0.15	Pyrogenic
	Spring	3.57	Biogenic	0.38	Pyrogenic
	Summer	1.77	Petrogenic	0.29	Pyrogenic
Station 3	Autumn	3.65	Biogenic	0.25	Pyrogenic
	Winter	2.70	Biogenic	0.27	Pyrogenic
	Spring	3.30	Biogenic	0.58	Pyrogenic
	Summer	1.65	Petrogenic	0.28	Pyrogenic



Chromatograms in certain water samples revealed the UCM zones (Figure 3).

Pollution indicators for PAHs:

The phenanthrene/anthracene ratios were employed to characterize the origins of PAH compounds found in water samples. Table Three. Because only a small number of water samples contained both fluoranthen and pyrene, and most had undetectable amounts of both, the ratio of fluoranthen to pyrene was harmful. Petrogenic is the source, as shown by the ratio values, which were smaller than one number at each station and, consequently, the ratio's overall values (for all stations during the period under analysis) (1).

Table (3): Water samples from the stations under observation during the study period were evaluated for the presence of aromatic chemicals and their originating source.

Stations	Seasons	LMW/HMW	Descriptions	Phen/Anth	Descriptions
Station 1	Autumn	0.30	Pyrogenic’	4.30	Pyrogenic’
	Winter	0.10	Pyrogenic’	2.50	Pyrogenic’
	Spring	0.17	Pyrogenic’	5.56	Pyrogenic’
	Summer	0.15	Pyrogenic’	0.80	Pyrogenic’
Station 2	Autumn	0.32	Pyrogenic’	2.49	Pyrogenic
	Winter	0.30	Pyrogenic’	6.17	Pyrogenic
	Spring	0.15	Pyrogenic’	3.33	Pyrogenic
	Summer	0.15	Pyrogenic’	0.98	Pyrogenic
Station 3	Autumn	0.34	Pyrogenic’	3.02	Pyrogenic
	Winter	0.43	Pyrogenic’	18.00	Petrogenic
	Spring	0.18	Pyrogenic’	4.00	Pyrogenic
	Summer	0.14	Pyrogenic’	0.96	Pyrogenic

Discussion

Water containing N-alkanes:

An essential component of hydrocarbons, N-alkanes interact with the aquatic environment through various processes, including the biodegradation of plankton and aquatic plants, the biosynthesis of marine organisms, anthropogenic sources, and geochemical effects. The findings showed that there was a seasonal variation in the concentrations of n-alkanes in the water, with higher concentrations in the spring and lower concentrations in the summer. High summer temperatures accelerated the evaporation of low molecular weight hydrocarbons and encouraged a range of microbes to biodegrade organic compounds [15].

The water samples contained n-alkanes with lengths ranging from C7 to C38. According to earlier studies, C24 is the main location of bacterial activity [16,17]. Even carbon number chains were found in water samples from C18–C26. Land plant chlorophyll has large molecular weight n-alkanes that may.

Water containing PAHs:

The direct sources of PAHs entering surface water include shipping, air-water exchange, and dry and wet atmospheric deposition. Pyrolysis and combustion activities account for the majority of these sources could be. Together, these impacts reduce the concentration of PAH chemicals, increasing the prevalence of low molecular weight PAHs in surface water. This may also be due to the degradation of low molecular weight PAHs in the water column [19]. There were two main types of PAH compounds found in the water.

Table (4): Comparison of dissolved PAHs (ng/l) and n-alkanes (μg/l) in water. Particulate) for the current study together with the others that have already been examined.

Studied Areas	n-alkane in water (μg/l)	PAHs in water (ng/l)	References
Shatt Al-Arab	6.50-14.23	7.19-22.47	[20]
Shatt Al-Arab	6.43 - 73.95	0.14 -31.91	[19]
Shatt Al-Arab	8.81″ – 35.58′	5.81 – 47.96″	[16]

Al-Chibayish marsh	0.32 – 2.98	2.435 – 37.780	[15]
River in BasraGovernorate, southern Iraq	0.877 – 13.462	0.046 – 2.494	[21]
some rivers in Misan Province,	-	1667.15 – 5552.7	[22]
Shatt Al-Arab, Basra, Southern Iraq	-	5.085 – 30.255	[23]
Tigris, Shatt Al Arab, Euphrates	48.09 – 276.98	45.16 – 1848.54	Current Study

Indexes of hydrocarbon sources:

The LMW/HMW ratio revealed both petrogenic and biogenic sources for n-alkanes. As most CPI ratios show, the ratio of two isoprenoids, phytane to pristane, is another useful indicator of the alkane's pyrogenic origin. In contrast to phytone (2, 6, 10, 14 tetramethylhexadecane), which is thought to be a characteristic of oil, pristane (2, 6, 10, 14-tetramethylpentadecane) is typically found in zooplankton and other animals [24].

According to the ratios of LMW/HMW, Flouranthen/Pyren, and Phenanthrene/Anthracen, most PAHs originate from pyrogenic and petrogenic sources and are undetected biogenic

Conclusion

1. The study discovered that petrogenic and pyrogenic sources are the two primary sources of aliphatic (n-alkane) hydrocarbons.
2. Polycyclic aromatic hydrocarbons with a low molecular weight Most polycyclic aromatic hydrocarbons come from petrogenic sources because they are more prevalent there than in pyrogenic ones.

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References

[1] I. C. Ossai, et al., "Remediation of Soil and Water Contaminated with Petroleum Hydrocarbon: A Review," Environmental Technology & Innovation, vol. 17, p. 100526, 2020.

[2] S. J. Varjani, "Microbial Degradation of Petroleum Hydrocarbons," Bioresource Technology, vol. 223, pp. 277–286, 2017.

[3] A. O. Adeniji, O. O. Okoh, and A. I. Okoh, "Petroleum Hydrocarbon Profiles of Water and Sediment of Algoa Bay, Eastern Cape, South Africa," International Journal of Environmental Research and Public Health, vol. 14, no. 10, p. 1263, 2017.

[4] B. Basumatary, et al., "A Study on Concentration of Total Petroleum Hydrocarbons in Lentic Water Bodies Near Oil Field Areas of Upper Assam, India," Journal of Environmental Biology, vol. 38, no. 3, pp. 375–382, 2017.

[5] G. Shamilishvily, E. Abakumov, and D. Gabov, "Polycyclic Aromatic Hydrocarbon in Urban Soils of an Eastern European Megalopolis: Distribution, Source Identification and Cancer Risk Evaluation," Solid Earth, vol. 9, no. 3, pp. 669–682, 2018.

[6] M. M. Al-Hejuje, N. A. Hussain, and H. T. Al-Saad, "Total Petroleum Hydrocarbons (TPHs), n-Alkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in Water of Shatt Al-Arab River–Part 1," Global Journal of Biology, Agriculture and Health Sciences, vol. 4, pp. 88–94, 2015.

[7] A. A. Lafta, "Estimation of Tidal Excursion Length Along the Shatt Al-Arab Estuary, Southern Iraq," Vietnam Journal of Science and Technology, vol. 59, no. 1, pp. 79–89, 2021.

[8] S. Mitra, et al., "Characterization, Source Identification and Risk Associated with Polyaromatic and Chlorinated Organic Contaminants (PAHs, PCBs, PCBzs and OCPs) in the Surface Sediments of Hooghly Estuary, India," Chemosphere, vol. 221, pp. 154–165, 2019.

[9] D. Han and M. J. Currell, "Persistent Organic Pollutants in China's Surface Water Systems," Science of the Total Environment, vol. 580, pp. 602–625, 2017.

[10] H. Shen, et al., "Global Atmospheric Emissions of Polycyclic Aromatic Hydrocarbons From 1960 to 2008 and Future Predictions," Environmental Science & Technology, vol. 47, no. 12, pp. 6415–6424, 2013.

[11] A. A. Talal, A. Y. Al-Adhub, and H. T. Al-Saad, "Seasonal and Regional Variations of Hydrocarbon Levels and Origin of n-Alkanes in Water of Southern Marshes of Iraq," Basrah Journal of Science (Bas J Sci), vol. 28, no. 2B, 2010.

[12] O. E. Fagbote and E. O. Olanipekun, "Characterization and Sources of Aliphatic Hydrocarbons of the Sediments of River Oluwa at Agbabu Bitumen Deposit Area, Western Nigeria," Journal of Scientific Research and Reports, vol. 2, no. 1, pp. 228–248, 2013.

[13] M. M. Al-Hejuje, N. A. Hussain, and H. T. Al-Saad, "Total Petroleum Hydrocarbons (TPHs), Alkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in Water of Shatt Al-Arab River–Part 1," Global Journal of Biology, Agriculture and Health Sciences, vol. 4, pp. 88–94, 2015.

[14] F. Kafilzadeh, A. H. Shiva, and R. Malekpour, "Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediments of the Kor River, Iran," Middle-East Journal of Scientific Research, vol. 10, no. 1, pp. 1–7, 2011.

[15] R. S. K. Al-Atbee, "Assessment of Some Heavy Elements and Hydrocarbons in the Water, Sediments and Dominant Aquatic Plants at Al-Chibayish Marshes," M.Sc. thesis, Dept. of Biology, Univ. of Basrah, Iraq, 2018.

[16] F. M. H. Al-Khatib, "Determination of the Concentrations, Origin and Distribution of Hydrocarbon Compounds in Water, Sediments and Some Biota of Hour Al-Hawaiian, South of Iraq and Their Sources," M.Sc. thesis, Dept. of Science, Univ. of Basrah, Iraq, 2008.

[17] H. T. Al-Saad, "Distribution and Sources of Hydrocarbons in Shatt Al-Arab Estuary and NW Arabian Gulf," Ph.D. dissertation, Univ. of Basrah, Iraq, 1995.

[18] H. Shen, et al., "Global Atmospheric Emissions of Polycyclic Aromatic Hydrocarbons From 1960 to 2008 and Future Predictions," Environmental Science & Technology, vol. 47, no. 12, pp. 6415–6424, 2013.

[19] M. F. H. Al-Bidhani, "Qualitative Composition of Phytoplankton in the Shatt Al-Arab and the Impact of Environmental Factors on the Production and Accumulation of Hydrocarbon Compounds," Ph.D. dissertation, Dept. of Biology, Univ. of Basrah, Iraq, 2014.

ISSN 3063-8186. Published by Universitas Muhamamdiyah Sidoarjo

https://doi.org/10.21070/ijhsm.v2i1.99

[20] W. A. Farid, et al., "Distribution, Sources, and Seasonal Variations of Hydrocarbons in Shatt Al-Arab River Water," Journal of International Academic Research for Multidisciplinary, vol. 2, no. 2, pp. 729–739, 2014.

[21] H. A. T. Malak, "Assessment of Environmental Pollution With Heavy Metals and Hydrocarbon Compounds in the Water and Sediments of the Abu Al-Khasib River in Basra Governorate, Southern Iraq," M.Sc. thesis, Dept. of Geology, Univ. of Basrah, Iraq, 2021.

[22] S. H. Jazza and A. A. Khwedem, "Origins and Distribution of Polynuclear Aromatic Hydrocarbons (PAHs) in Water and Sediments of Some Rivers in Misan Province, Iraq," Iranian Journal of Ichthyology, vol. 8, pp. 46–53, 2021.

[23] B. M. Younus and H. M. Younis, "The Impact of Population and Industrial Waste on the Waters of the Shatt Al-Arab, Basra, Southern Iraq," Central Asian Journal of Medical and Natural Science, vol. 4, no. 4, pp. 619–632, 2023.

[24] J. M. Guerra-García, F. J. González-Vila, and J. C. García-Gómez, "Aliphatic Hydrocarbon Pollution and Macrobenthic Assemblages in Ceuta Harbour: A Multivariate Approach," Marine Ecology Progress Series, vol. 263, pp. 127–138, 2003.