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PAH Distribution and Combustion Sources in Tigris River Sediments

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Abstract

General Background Polycyclic aromatic hydrocarbons are persistent organic pollutants that accumulate in aquatic sediments and pose ecological and health risks. **Specific Background** The Tigris River at Amara City is exposed to urban, industrial, and hydrological pressures that may promote PAH accumulation. **Knowledge Gap** However, detailed information on PAH concentrations and sources in this river section remains limited. **Aims** This study aimed to assess the concentration, spatial distribution, and sources of PAHs in surface sediments along the Tigris River at Amara City. **Results** Sediment samples from five stations were analyzed using GC–MS, revealing total PAH concentrations ranging from 2.73 to 206.05 ng/g, with a pronounced hotspot at Station 5. High molecular weight PAHs dominated most stations, and diagnostic ratios indicated predominantly pyrogenic sources, with minor petrogenic input at one station. **Novelty** This study provides site-specific evidence of localized PAH contamination and source patterns within a critical reach of the Tigris River. **Implications** The findings offer baseline data for environmental monitoring and support pollution management strategies in southern Iraq.

Keywords:

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Keywords:

PAHs, River Sediments, GC–MS Analysis, Source Identification, Tigris River

Key Findings Highlights:

1. Marked spatial variability in sediment contamination was observed among sampling stations.
2. Combustion-derived compounds dominated most sampling locations.
3. A localized hotspot exhibited elevated carcinogenic compound levels.

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of persistent organic pollutants characterized by two or more fused aromatic rings. They originate primarily from incomplete combustion of organic matter (e.g., fossil fuels, biomass, waste) and pyrogenic sources (e.g., industrial processes, vehicle emissions), as well as petrogenic sources like crude oil spills and natural seeps (The most important source of aromatic hydrocarbons is gaseous waste from oil fields) [1]. Due to their hydrophobic nature and low solubility, PAHs readily adsorb to suspended particles and accumulate in aquatic sediments, acting as long-term reservoirs of contamination [2]. This persistence poses significant ecological and human health risks, as many PAHs are carcinogenic, mutagenic, and toxic to aquatic organisms [3].

The Tigris River, a vital freshwater resource in Iraq, sustains agriculture, industry, and domestic needs along its course. At Amara City in southern Iraq, the river is exposed to multiple anthropogenic pressures. Rapid urbanization, industrial discharges, untreated municipal sewage, agricultural runoff, vehicular emissions, and historical conflict-related pollution contribute) damage caused by historical political, military, or social conflicts in the region, which have indirect but severe environmental consequences. These conflicts often lead to poor infrastructure maintenance, particularly drainage systems, resulting in inadequate wastewater management and increased pollutant discharge into water bodies(. Human activities, such as unauthorized dumping, intensified agriculture, and industrial neglect during and after conflicts, exacerbate the pollution load. The cumulative effect is significant environmental degradation affecting water and sediment quality to the degradation of water and sediment quality [4]. Additionally, reduced river flow due to upstream damming exacerbates pollutant accumulation in sediments. These factors create a critical need to assess sediment contamination, as sediments reflect historical and ongoing pollution and can release toxins back into the water column under changing conditions [5].

Monitoring PAHs in the sediments of the Tigris River at Amara City is essential for several reasons: (1) identifying contamination hotspots and sources; (2) evaluating ecological risks to benthic organisms; (3) informing public health strategies for communities relying on the river; and (4) guiding remediation efforts. Despite its importance, comprehensive data on PAH levels in this specific reach of the Tigris remains limited. This study therefore aims to quantify the concentration, composition, and spatial distribution of PAHs in sediment samples collected from the Tigris River at Amara City, southern Iraq. Consequently, this finding will contribute to a baseline understanding of contamination, support ecological risk assessments, and aid in developing targeted management strategies for this crucial ecosystem.

Materials and Methods

Study Area and Sampling Stations

Five stations were selected along the Tigris River at Amara City, Maysan Province (Fig 1, Table 1). Samples were collected systematically to represent riverine conditions affected by urban and industrial inputs.

Analytical Methods

Sedimentsamples were dried in an oven at 50 °C, grinded finely in an electrical mortar and sieved through a 63 µm mesh sieve, stored in glasses containers until analysis. 50 grams of sieved sediment were placed in cellulose thimble and extracted by using Soxhlet intermittent extraction according to the method of Goutx and Saliot, 1980 and Saleh et al., 2021 [6][7] by adding a mixture of solvents (120 ml) methanol: benzene (1:1 v/v) for 48 hrs. at temperature doesn't exceed 40^{o}C. The combined extracts were saponification for 2 hrs. by adding (15ml) 4M MeOH (KOH) at the same temperature and cooled to room temperature. The un saponification matter was extracted with (50 ml) n-hexan using separator funnel. a 20 cm glass column packed with glass wool, 8 g silica gel (100-200 mesh), 4 g aluminum oxide (Al_2O_3, 100-200 mesh), and 4 g anhydrous sodium sulfate (Na_2SO_4) at the top. The Aromatic component was eluted by using benzene.

GC-MS examination of PAH compounds was performed using an Agilent 7890B gas chromatograph interfaced with an Agilent 5977A mass spectrometer. The temperature schedule of the GC oven was: starting temperature of 40°C, ramped at a rate of 10°C/min to a final temperature of 310°C. The injector temperature was set to 260°C by employing split mode (ratio 75:1). The flow control was set to constant flow with the pressure of 7.0699 psi, total flow of 79 mL/min, column flow of 1 mL/min, and purge flow of 3 mL/min.

Mass spectrometer conditions: ion source temperature 250°C, quadrupole temperature 150°C, interface temperature 280°C. Solvent cut time was constant at 4.00 minutes, with start time 4.00 minutes and end time 35.00-40.00 minutes. Individual PAH compounds were identified by comparison of retention times and mass spectra with authentic standards and the NIST mass spectral library. Quantification was done by external standard calibration using PAH standards.

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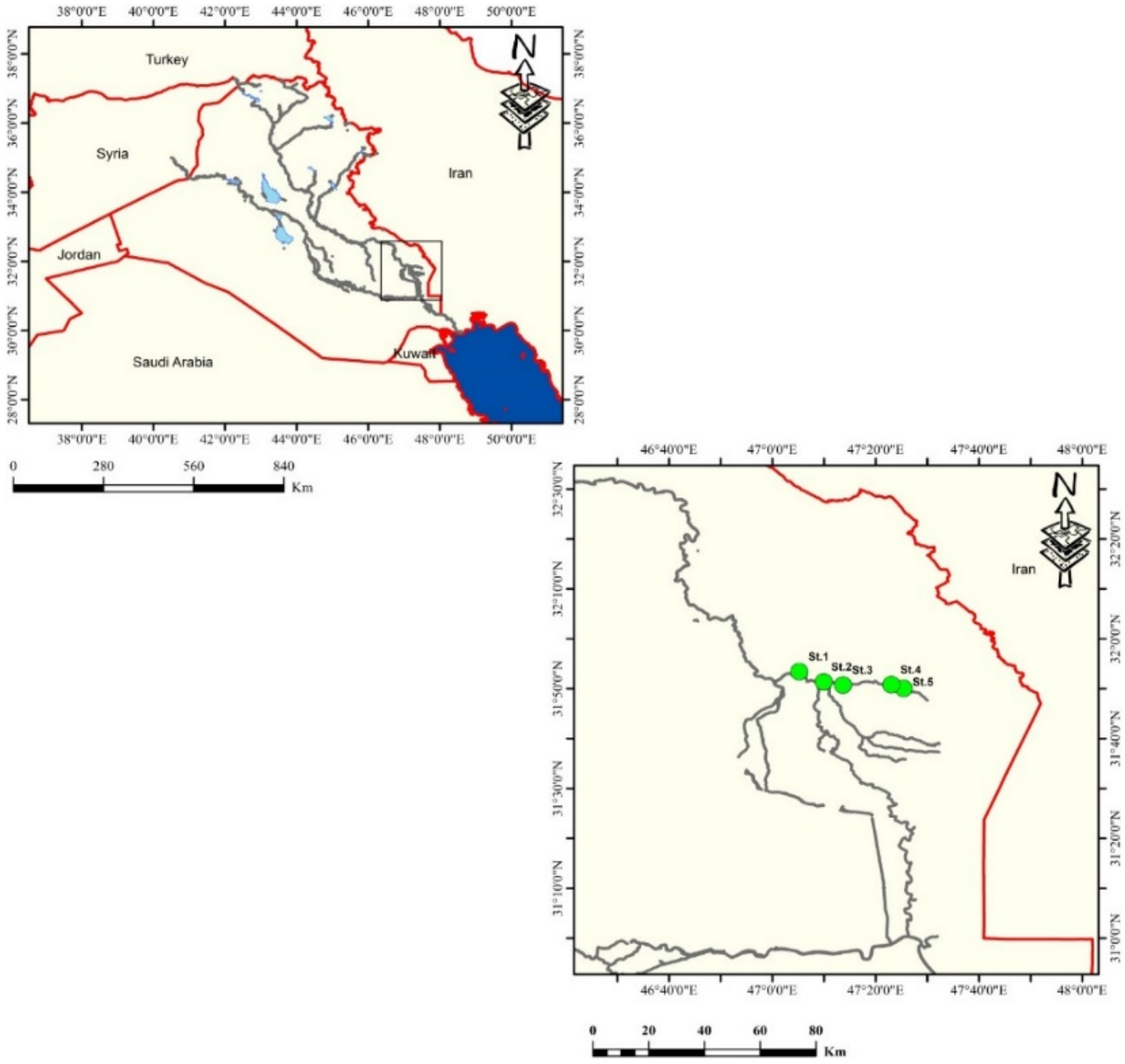

Figure 1. **Fig(1) sample location sites**

Station	Location
St1	31.894134°,47.092327°
St2	31.854351°,47153420°
St3	31.858358°, 47.180358°
St4	31.849643°, 47.365625°
St5	31.834767°, 31.834767°

Table 1. Table (1) the GIS position of the sampling stations

Results and Discussion

The attached data in table 2 presents the concentration and distribution of PAH compounds in five stations at Messan governorate, Total PAH levels ranged from 2.73 to 206.04 ng/g dry weight.

In addition, Table 2 shown the High molecular weight of PAHs (HMW-PAHs, 4–6 rings) dominated all stations, while low molecular weight (LMW-PAHs) was minor. The LMW/HMW ratio was consistently less than 1 across all stations, indicating a predominance of combustion-related (pyrogenic) and oil-derived (petrogenic) sources as shown in table 2 at st_3, moreover

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the Fl/Py> 1 also supports this conclusion. Mixed industrial and traffic-related sources are common at Amara City Context: While specific Amara studies are limited, its status as a major southern city suggests levels likely fall between moderately contaminated rural areas and highly contaminated at Amara. Expected ΣPAHs could range from hundreds to potentially low thousands of ng/g dw, influenced by local sources like municipal waste, vehicle emissions, and possible agricultural burning.

Rural/Upstream Areas: Lower concentrations are typically found upstream of major cities and in less industrialized stretches. Values often range from <100 to 500 ng/g dw ΣPAHs [8].

Low molecular weight (LMW) PAHs (e.g., Naphthalene, Acenaphthene, Fluorene) are consistently present at lower levels across all stations. The total PAH concentrations increase downstream, peaking at Station 5, then slightly decreasing at all Stations.

At the level of individual hazardous PAH compounds, Station 5 exhibited higher concentrations than the other stations. The recorded values were 1.014 ng/g for anthracene, 2.340 ng/g for fluoranthene, 1.338 ng/g for pyrene, 27.702 ng/g for benzo(a)fluoranthene, 24.952 ng/g for benzo (b + k) fluoranthene, 78.586 ng/g for dibenzo(a)pyrene, 13.563 ng/g for indeno(1,2,3-cd) pyrene + dibenzo(a,h)anthracene, and 46.832 ng/g for benzo(g,h,i) perylene. In contrast, the highest concentration of chrysene (23.847 ng/g) was observed at Station 1, this could be due to a major point source nearby, such as intense industrial discharge (e.g., heavy industry, power generation), a major municipal wastewater outfall with high solids loading, or historical accumulation from intense combustion activities. The dominance of carcinogenic 5- and 6-ring PAHs (BaF, BbF, BkF, DahA, IcdP, BghiP) at St5 is particularly alarming due to their high toxicity and persistence [9].

High Molecular Weight (HMW) PAHs Dominate: 4-, 5-, and 6-ring PAHs (e.g., Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd] pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene) are generally the most abundant and concerning fractions due to their higher carcinogenicity [7].

Moreover, the minor Petrogenic Inputs: Lower molecular weight PAHs (e.g., Phenanthrene, Fluoranthene relative to Benzo[a]pyrene) and ratios like LMW/HMW PAH sometimes indicate minor contributions from petroleum spills or uncombusted fossil fuels in specific locations, like near refineries or oil terminals [8].

The construction of upstream dams—particularly in Turkey—has markedly decreased the discharge of the Tigris River within Iraq. Reduced flow intensifies pollution impacts by limiting dilution capacity and prolonging the residence time of contaminants, which promotes their accumulation in river sediments. This effect is especially pronounced in the southern, low-velocity reaches of the river, such as the area near Amara [10]. In addition, contaminant concentrations exhibit notable seasonal variability. Elevated levels are commonly recorded during dry periods due to diminished river discharge, reduced dilution, and enhanced particle deposition. In contrast, flood events may resuspend contaminated sediments while temporarily lowering concentrations through increased dilution [11].

PAH compounds	St_1	St_2	St_3	St_4	St_5
Acenaphthylene	0	0	0	0.03008475	0
Acenaphthene	0	0	0	0.03156675	0.03539275
Fluorene	0	0	0.03249825	0.039469	0.07498775
Phenanthrene	1.20157	0.10859575	0.14015375	0.492035	1.0144925
Anthracene	0.56505	0.0946	0.025375	0.4113425	1.0148875
Fluoranthene	0.2151305	0.9877725	0.2164415	0.0232616	2.3408525
Pyrene	0.09031225	0.0766795	0.04872925	0.0386975	1.33867
Benzo(a)fluoranthene	0.5065125	0.4614325	0.0264565	0.0309435	27.70263
Chrysene	23.847215	3.0824175	0.5634825	0.632965	8.5894625
Benzo(b)fluoranthene Benzo(k)fluoranthene	0.922275	0.4761525	0.2738375	0.13885075	24.952395
Dibenzo(a) pyrene	2.2967425	1.396275	1.426015	0.4492375	78.586815
Indenol(1,2,3-cd) pyrene+Dibenz (a, h) anthracene	0.29924	0.10177525	0.45424	0.3606275	13.563325
Benzo (g, h,i)perylene	0.2065975	0.27501	0.39983	0.05474075	46.8324625
Total	30.15064525	7.0607105	3.60705925	2.7338221	206.046373
LMWPH	1.767	0.203	0.198	1.001	2.140
HMWPH	28.384	6.858	3.409	1.729	203.905
LMWPH/HMWPH	0.062	0.030	0.058	0.581	0.011
Phenanthrene/ Anthracene	2.127	1.148	5.523	1.196	0.999
Fluoranthene/Pyrene	2.382	12.882	4.442	0.601	1.749
Anthracene/ (Anthracene + Phenanthrene)	0.320	0.270	0.153	0.455	0.500

Table 2. **Table 2 : Individual PAH Concentrations (ng/g dry weight) at each station**

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A strong positive relationship is evident between downstream proximity and polycyclic aromatic hydrocarbon (PAH) contamination. The highest total PAH concentration was recorded at Station 5 (St5; ∑PAHs 206.05 ng/g), representing a pronounced outlier and indicating the presence of intense, localized pollution sources, such as industrial effluents or urban runoff. Table 3 shown the origin of PAHs according to diagnostic ratio analysis revealed a predominance of pyrogenic sources across most stations (St1–St3 and St5), characterized by elevated high-molecular-weight (HMW) PAHs associated with combustion processes. In contrast, Station 3 exhibited a petrogenic signature, likely reflecting inputs from unburned petroleum hydrocarbons the references of these classifications illustrated at Table 5. Station 4 showed the lowest ∑PAHs value (2.73 ng/g), with dominance of low-molecular-weight (LMW) compounds, suggesting minimal anthropogenic influence [12]. From an ecological perspective, the elevated levels of carcinogenic HMW PAHs at St5, including benzo(a)fluoranthene and dibenzo(a)pyrene, pose significant environmental and health risks and therefore warrant immediate attention (e.g., Shatt al-Arab studies) [13]. Figure 2 illustrates the percentage distribution of PAHs in the study area, showing the high proportion of polycyclic aromatic compounds at station 5.

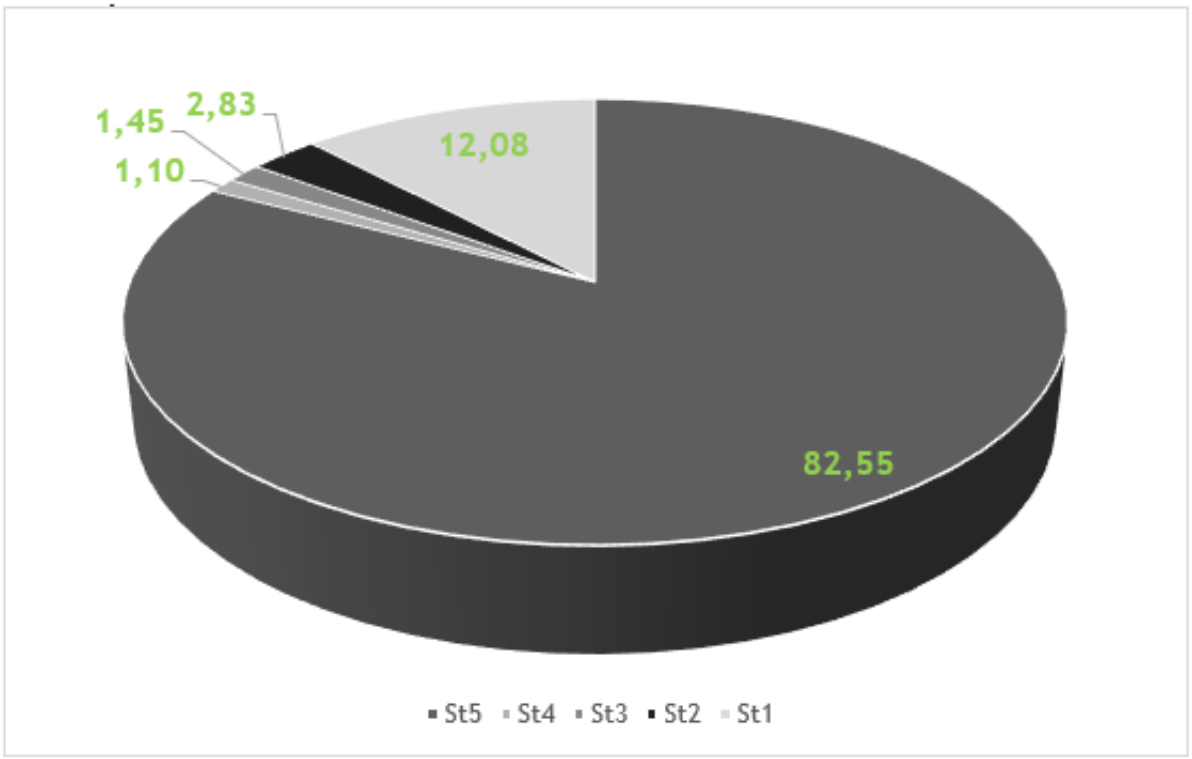

Figure 2. **Fig (2) Percentage of ∑PAHs in each station**.

The table 3 represents the classification ranges of PAHs based on the criteria of Baumard et al. [14]. According to this classification, sediments at Station (St5) fall within the moderately polluted category, whereas sediments from the remaining stations are characterized by low levels of contamination.

Standard / Source	Classification Range	Interpretation