

# Spatiotemporal distribution and risk assessment of polycyclic aromatic hydrocarbons in the Tigris River near Baghdad Medical City wastewater discharge

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are persistent, carcinogenic contaminants. We tracked the 16 U.S. Environmental Protection Agency (EPA) priority PAHs in surface waters of the Tigris River at five stations spanning 100 m upstream to 1.5 km downstream of Baghdad Medical City's wastewater outfall during October 2024, January 2025, and April 2025. Samples underwent liquid–liquid extraction (LLE), copper desulfurization, and gas chromatography with flame-ionization detector (GC-FID) analysis. Total PAH concentrations ( $\Sigma 16$  PAHs) peaked at the sewer outlet in all seasons (up to  $31 \mu\text{g L}^{-1}$ ) and declined at 1.5 km downstream to levels close to the pre-sewage discharge point. Site explained 93.75% of the spatiotemporal variance ( $p < 0.001$ ). The share of high-molecular-weight PAHs rose from 48% at the outfall to 67% after 1.5 km. Total risk quotient ( $\Sigma\text{RQ}$ ) peaked at  $2.5 \times 10^3$  in January, exceeding the safety threshold, while benzo[a]pyrene-equivalent toxicity (BaP-TEQ) peaked at  $1.9 \mu\text{g BaP eq L}^{-1}$ . Winter benzo[a]pyrene ( $0.262 \mu\text{g L}^{-1}$ ) exceeded Dutch and Canadian aquatic criteria by 17–26-fold. Diagnostic ratios trace the origin of PAHs to medical waste and biomass combustion

**Keywords:** benzo[a]pyrene, biomass combustion, diagnostic ratios, polycyclic aromatic hydrocarbons, risk quotient, Tigris River, wastewater.

## INTRODUCTION

The Tigris River, one of Iraq's two main rivers, flows through Baghdad City for approximately 60 km, mostly within urban areas (Asaad and Abed, 2020). Rapid urbanization, diffuse agricultural runoff, and chronically underperforming wastewater infrastructure have already driven several physico-chemical parameters beyond Iraqi and World Health Organization (WHO) limits, signaling a steady decline in water quality (Grmasha et al., 2023). In large cities such as Mosul, up to  $400,000 \text{ m}^3 \text{ day}^{-1}$  of untreated domestic, industrial, and hospital effluent are discharged daily into the Tigris River, severely burdening the river's ecological system and compromising water quality (Hmoshi et al., 2024). Due to a lack of proper guidelines and infrastructure, hospital waste is generally mixed with municipal waste, which makes segregation and

disposal even more difficult and dangerous (Hassan and Mahmood, 2019; Al-Hiyaly et al., 2016). Consumption of substandard drinking water elevates population-level health risks and, consequently, escalates healthcare expenditures (Al-Dhamin, 2023). wastewater can be the source of aromatic compounds that can enter the river and pose risk to aquatic organisms (Ahmed et al., 2021). Polycyclic aromatic hydrocarbons (PAHs) are among the key aromatic organic pollutants found in both medical waste and municipal wastewater due to their widespread generation from incomplete combustion processes and organic chemical discharge (Patel et al., 2020; Kurwadkar et al., 2022). PAHs are divided into low-molecular-weight (LMW) with 2 to 3 benzene rings and 4 to 6 rings high-molecular-weight (HMW) based on their structure and properties (Hassan et al., 2019). Studies indicate that more toxic compounds can form from reactions of

low molecular weight PAHs with other pollutants, such as nitrated and oxy-PAHs (Peng et al., 2023). HMW PAHs are persistence in the environment, known to be associated with severe toxicological effects, including carcinogenicity and mutagenicity (Juda et al., 2019). Incomplete incineration of plastic-based medical supplies has increased the proportion of synthetic polymers, along with pharmaceutical formulations and laboratory solvents used in large hospital complexes, generating polycyclic aromatic hydrocarbons (PAHs), which are hydrophobic and carcinogenic compounds (Srivastava et al., 2024; Agarwal et al., 2024; Montano et al., 2025). PAHs are on the short list of substances for which all significant regulators worldwide have already established binding water limits due to clear evidence of genotoxicity and cancer risk. The Guidelines of the World Health Organization for Drinking Water Quality retain a health-based value of  $0.7 \mu\text{g L}^{-1}$  for benzo[a]pyrene, the sentinel PAH used as a proxy for the group (WHO, 2022). The European Union's Water Framework Directive goes further: Directive 2013/39/EU identifies four harmful PAHs: benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), and indeno[1,2,3-cd]pyrene (Ind[1,2,3-cd]P) as important substances, setting a safe limit of  $0.05 \mu\text{g L}^{-1}$  for BaP in rivers and lakes. The Safe Drinking Water Act in the United States sets a mandatory maximum contaminant level (MCL) of  $0.2 \mu\text{g L}^{-1}$  for BaP and an MCL goal of zero (EP & CEU, 2013; U.S. EPA, 2024). Recent human studies show that greater daily PAH intake is associated with higher levels of BaP–DNA (BPDE) adducts, an established biomarker linked to cancer risk (Guo et al., 2024). Additionally, even minimal concentrations of BaP in water, such as  $0.1 \mu\text{g L}^{-1}$ , caused developmental stress in some aquatic organisms (Xu et al., 2023). This study investigates the distribution and risks of polycyclic aromatic hydrocarbons (PAHs) along the Baghdad Medical City outfall transect. It measures all 16 EPA priority PAHs shown in Table 1, at five sampling points (–100 m, 0 m, +100 m, +500 m, +1500 m) across three seasons: autumn 2024, winter 2025, and spring 2025. Spatial and seasonal variations are evaluated using Kruskal–Wallis test, while a comprehensive set of diagnostic molecular ratios is applied to identify PAH sources and compare exposure levels with international health guidelines. Furthermore, ecological and human-health risks are assessed through the calculation of risk quotients (RQ) and toxic equivalency (TEQ) metrics.

**Table 1.** Abbreviations, full chemical names, and number of fused aromatic rings for the 16 U.S. EPA priority polycyclic aromatic hydrocarbons (PAHs) quantified in this study

Abbreviation	Full name	Number of rings
Nap	Naphthalene	2
Acy	Acenaphthylene	3
Ace	Acenaphthene	3
Flu	Fluorene	3
Phe	Phenanthrene	3
Ant	Anthracene	3
Flt	Fluoranthene	4
Pyr	Pyrene	4
BaA	Benz[a]anthracene	4
Chr	Chrysene	4
BbF	Benzo[b]fluoranthene	5
BkF	Benzo[k]fluoranthene	5
BaP	Benzo[a]pyrene	5
IcdP	Indeno[1,2,3-cd]pyrene	6
DBA	Dibenzo[a,h]anthracene	5
BghiP	Benzo[ghi]perylene	6

## MATERIALS AND METHODS

### Study area and sampling sites

Baghdad Medical City is a 3,000-bed healthcare complex in Baghdad, Iraq ( $33^{\circ}20'49''$  N,  $44^{\circ}22'44''$  E. that releases mixed hospital wastewater through an underground gravity conduit directly into the Tigris River. Moreover, multiple investigations have shown that this untreated discharge elevates heavy metal loads (Abd Al-Satar and Sachit, 2021). and microbial indicators (Olewi and Al-Dabbas, 2022), within the first few hundred meters downstream of the outfall. Five sampling stations were therefore established along the thalweg, as summarized in Table 2: a control 100 m upstream of the outfall (S1, –100 m); the effluent pipe itself (S2); and three downstream points (S3, +100 m), (S4, +500 m), and (S5, +1500 m). to minimize bank-side bias and ensure adequate grab sampling depth, all sites were mid-channel (~15 m from either bank) except for S2 in which the sampling was directly from the effluent pipe. Figure 1 shows Study area Map and Sampling Sites.

### Sampling design

Water was collected during three seasons: October 2024, January 2025, and April 2025. At

each station, Grab samples were collected at 50cm depth using 1 L amber borosilicate glass bottles. Bottles were pre-cleaned following APHA Standard Methods: washed with laboratory-grade detergent, rinsed with deionized water, and flushed with acetone and n-hexane to eliminate organic residue (Lee et al., 2023; Baird et al., 2017). Bottles were air-dried, sealed with ground-glass stoppers, and rinsed three times with site water before sampling. To minimize oxidative loss of polycyclic aromatic hydrocarbons (PAHs), samples were collected without agitation, leaving no air headspace, and dosed in situ with sodium thiosulfate at a concentration of 80 mg L<sup>-1</sup> (ISO, 2024).

### Laboratory analysis

Water samples were processed within seven days of collection using a liquid–liquid extraction method (Chen et al., 2019). An aliquot of 100 mL homogenized water sample was transferred into a clean glass tube and mixed with 30 mL of a mixture of acetone and n-hexane (1:1, v/v). The mixture was vortexed for 1 minute and subjected to ultrasonic treatment for 15 minutes to enhance phase contact and extraction efficiency. Samples were centrifuged for 10 minutes at 3000 rpm to separate the organic phase from the aqueous phase. The upper organic phase was collected with a Pasteur pipette, and the aqueous phase was re-extracted twice with 10 mL portions of acetone: n-hexane (1:1). All organic extracts were combined, treated with activated copper to remove elemental sulfur, and dried over anhydrous sodium sulfate. The eluate was further concentrated to 1mL using the rotary evaporator, transferred to amber GC vials, and subsequently refrigerated at 4 °C before analysis. The investigation was conducted at the laboratories of the Ministry of Science and Technology, at the Food Research Centre, Baghdad /Iraq, using a Shimadzu GC-2010 gas chromatograph (Japan).

### Quality control

External standard techniques were used to establish the quantitative standards for the 16 PAHs present in the water sample. The linearity correlation for 16 PAHs was 0.997. Analyte concentration was used to determine the limits of detection (LOD), which were then calculated using a three-fold signal-to-noise ratio (Zhang et al., 2022). The LOD range for water was 0.06 µg L<sup>-1</sup>. Each sample was tested in triplicate using a method blank (solvent), a spiked blank (standards added to solvent), and a sample. There was no discernible PAH contamination, as indicated by method blank analysis.

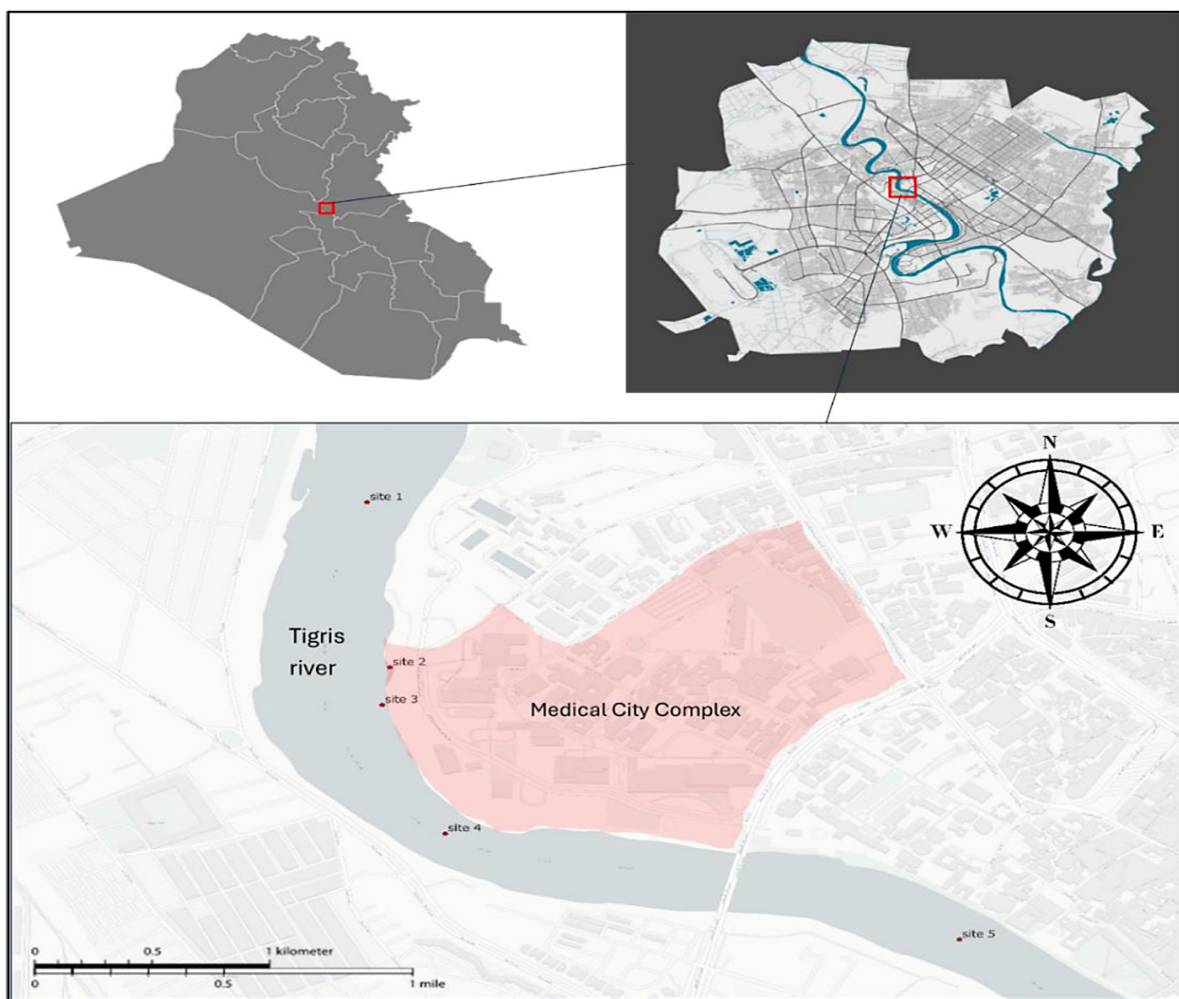
## RESULTS AND DISCUSSION

### Overview

Sixteen PAH congeners were quantified at all five stations in October 2024, January 2025, and April 2025. Concentrations of the summed 16 compounds (Σ16PAH) shown in Table 3, ranged from 3.52 µg L<sup>-1</sup> at the upstream background (S1, January) to 30.98 µg L<sup>-1</sup> at the Medical-City wastewater outfall (S2, January). Although lower than the historic Shatt Al-Hilla spike 602 µg L<sup>-1</sup> (Hussein et al., 2014), and peaks of 327 and 279 µg L<sup>-1</sup> by (Zaki et al., 2025), and (Al-Azawii et al., 2015), respectively. this value still places the Medical-City outfall among the highest BaP records for Iraqi freshwaters and signals chronic ecological risk. The winter maximum of benzo[a]pyrene at S2 0.262 µg L<sup>-1</sup> exceeds the Dutch negligible concentration criterion 0.010 µg L<sup>-1</sup> by 26 x and the Canadian Council of Ministers of the Environment (CCME) aquatic life guideline 0.015 µg L<sup>-1</sup> by 17 x. A one-way ANOVA revealed a highly significant spatial variation in total PAHs among the five sampling sites ( $F_{4,10} = 37.57$ , p

**Table 2.** Geographic coordinates and spatial distribution of sampling sites along the Tigris River near Baghdad Medical City

Sites	Site description	Longitude	Latitude
Site-1	500 m upstream of the discharge point	44°22'19.0"E	33°21'05.8"N
Site-2	Discharge point	44°22'22.2"E	33°20'52.1"N
Site-3	100 m downstream	44°22'19.7"E	33°20'47.9"N
Site-4	500 m downstream	44°22'25.1"E	33°20'37.3"N
Site-5	1500 m downstream	44°23'01.5"E	33°20'28.2"N



**Figure 1.** Study area map showing Baghdad Medical City and five PAH sampling sites along the Tigris River. Inset maps show the location of the study area within Baghdad and Iraq. SAGA GIS (Version 9.7.1) <https://saga-gis.sourceforge.io>

$< 0.001$ ). Post-hoc Tukey HSD analysis showed that Site 2 exhibited the highest total PAH concentration ( $28.17 \mu\text{g/L}$ ), significantly exceeding all other sites ( $p < 0.001$ ). Site 3 ( $17.83 \mu\text{g/L}$ ) was also significantly higher than Sites 1, 4, and 5, indicating that elevated PAH levels persist for at least 100 m downstream of the discharge. Sites 1 ( $4.75 \mu\text{g/L}$ ) and 5 ( $9.17 \mu\text{g/L}$ ) formed the lowest homogeneous subset, representing background or recovered water quality conditions. Site 4 ( $11.53 \mu\text{g/L}$ ) was positioned within an intermediate subset with moderate contamination. The spatial pattern followed the order  $S1 < S5 < S4 < S3 < S2$ , confirming the strong localized impact of the hospital effluent and partial downstream recovery. Homogeneous subset analysis supported this pattern, grouping S1 and S5 as low-PAH sites, S4 as moderate, and S3 and S2 as highly contaminated.

### Spatial patterns

Site S2, located at the effluent outfall, was the dominant hot spot in every season, with  $\Sigma 16\text{PAH}$  concentrations four to six-fold higher than those at the control S1 ( $23.58$  vs  $4.04 \mu\text{g L}^{-1}$  in October,  $30.98$  vs  $3.52 \mu\text{g L}^{-1}$  in January, and  $30.1$  vs  $6.69 \mu\text{g L}^{-1}$  in April). Approximately 100 m downstream, S3 recorded the second-highest values ( $15.62$ – $21.84 \mu\text{g L}^{-1}$ ), indicating rapid yet incomplete dilution of the wastewater. Stations S4 and S5, situated 500–1500 m downstream, carried intermediate loads of about  $8.06$ – $11.9 \mu\text{g L}^{-1}$ , still two to three times the rural background. This persistent spatial hierarchy  $S2 \gg S3 > S4 \approx S5 > S1$ , shows that proximity to the wastewater outlet, rather than season, governs absolute PAH concentrations in the reach. Across the five stations, a clear longitudinal shift from low to high-molecular-weight dominance emerges.



## Seasonal patterns

Mean concentrations of  $\Sigma 16$  PAH rose slightly from October ( $12.9 \mu\text{g L}^{-1}$ ) to January ( $13.8 \mu\text{g L}^{-1}$ ) and April ( $16.2 \mu\text{g L}^{-1}$ ). The outfall station (S2) displayed a clear winter maximum ( $30.9 \mu\text{g L}^{-1}$ ) with negligible spring decline, reflecting sustained effluent input. Immediately downstream (S3) concentrations were lowest in January ( $15.6 \mu\text{g L}^{-1}$ ) and 35% higher in April. The upstream control (S1) and far-field site (S5) likewise showed winter minima ( $3.52$  and  $8.06 \mu\text{g L}^{-1}$ ) and spring maxima ( $6.69$  and  $10.4 \mu\text{g L}^{-1}$ ), whereas the mid-reach station (S4) remained nearly constant ( $\sim 11$ – $12 \mu\text{g L}^{-1}$ ). Central-Baghdad reaches (urban Tigris) show winter maxima, driven by domestic heating (Mustafa et al., 2023), while cleaner rural tributaries often peak in spring due to reduced dilution.

## Composition of the 16 priority PAHs

### *LMW/HMW variation in the water column*

Because molecular weight governs solubility and breakdown rates, PAHs follow a predictable environmental pattern. Low molecular weight (2–3 ring) congeners stay relatively water soluble and are quickly lost through volatilization and microbial breakdown (Berríos-Rolón et al., 2025). High molecular weight (4–6 rings) PAHs, by contrast, are poorly soluble, less volatile, and more resistant to biodegradation; they sorb to particles and persist in river water and sediments even after LMW fractions have dissipated (Zhao et al., 2022). Spatial gradient based on annual means. By taking the mean values of HMW and LMW of all sites for each season as shown in Figure 2, the averaged  $\Sigma 16$ PAH at S1 is still slightly enriched in LMW compounds (53.8% of  $\Sigma 16$ PAH,  $2.56 \mu\text{g L}^{-1}$  on average), and at the Medical City outfall (S2), the profile is similar (LMW 52.78 %,  $14.9 \mu\text{g L}^{-1}$ ). Just 100 m downstream (S3), the balance tips as HMW species rise to 58% of the total and remain the controlling fraction further downstream, climbing to 64 % at S4 and 67% at S5. In absolute terms, the LMW load collapses by almost 80% between S2 ( $14.9 \mu\text{g L}^{-1}$ ) and S5 ( $3.0 \mu\text{g L}^{-1}$ ), whereas the HMW pool is only halved, from  $13.3 \rightarrow 6.1 \mu\text{g L}^{-1}$ . Together with the concurrent drop in  $\Sigma 16$ PAH concentrations  $28 \rightarrow 9 \mu\text{g L}^{-1}$ , this pattern indicates that lighter, more volatile and biodegradable PAHs are preferentially lost

during river transport, while 4–6 ring congeners persist and progressively dictate the mixture's toxic potential downstream. Seasonal shifts. Comparing according to seasonal variations, the LMW/HMW ratio at (S1) is always near parity yet trends slightly toward LMW in spring. LMW climbs from 52.7% (Oct) and 50.8% (Jan) to 56% (Apr). At S2, composition is remarkably constant, LMW hovers at  $52 \pm 1\%$  across all dates, even though the total mass peaks in January ( $31 \mu\text{g L}^{-1}$ ) and remains high in April. The source signature, therefore, appears stable and largely immune to seasonal hydrology. At S3, the January column still shows strong HMW dominance (62%), but by April the profile has flattened (HMW  $\approx 50\%$ ), driven by a two-fold rise in LMW load ( $10.94 \mu\text{g L}^{-1}$ ). Farther downstream at S4 and S5, the winter snapshot (Jan) is the most HMW skewed of the year (70.8% at S4 and 73% at S5). With spring flows, however, the balance swings: LMW shares jump to 45.1% (S4) and 43.1% (S5) in April, cutting the HMW dominance by about 20 percentage points while total PAH drops only modestly. High HMW shares are frequently linked to pyrogenic inputs such as diesel generators, incineration of clinical waste, and heavy traffic, whereas petrogenic releases tend to elevate LMW and 4-ring PAHs (Janneh et al., 2023).

### *Source identification of PAHs*

Diagnostic ratios were benchmarked against source-specific cut-off bands (Tobiszewski and Namieśnik, 2012), which classify PAH origins as petrogenic, vehicular, or biomass combustion without site-specific calibration, Table 4 shows the diagnostic-ratio ranges. The ring-class pattern reveals two dominant regimes: S2 (Medical City outfall) and S3 are consistently pyrogenic, while S1 shows a petrogenic background signal. S4 and S5 exhibit mixed signatures, shifting from pyrogenic in winter to more petrogenic in spring. At S2, all seasons fall within the combustion domain, with winter  $\text{Ant}/(\text{Ant} + \text{Phe}) = 0.20$ – $0.63$ ,  $\text{Flu}/(\text{Flu} + \text{Pyr}) = 0.28$ – $0.56$ , and  $\text{BaA}/(\text{BaA} + \text{Chr}) = 0.42$ – $0.56$ . Across stations, combustion dominates, but seasonal fingerprints vary. S1 shows low  $\text{Flu}/(\text{Flu} + \text{Pyr}) (<0.4)$  and  $\text{Ant}/(\text{Ant} + \text{Phe}) >0.10$  in October–January, shifting toward combustion by April ( $\text{Flu} > 0.40$ ). S2 and S3 remain unambiguously pyrogenic, with  $\text{Flu}/(\text{Flu} + \text{Pyr}) >0.50$  and  $\text{BaA}/(\text{BaA} + \text{Chr}) >0.35$ , while  $\text{IcdP}/(\text{IcdP} + \text{BghiP})$

**Table 3.** Descriptive statistics (mean  $\pm$  SD; range) for polycyclic aromatic hydrocarbon (PAH) concentrations ( $\mu\text{g L}^{-1}$ ) measured at Sites 1–5 along the study reach

PAHs		Site 1	Site 2	Site 3	Site 4	Site 5
Nap	Mean $\pm$ SD	0.58 $\pm$ 0.18	5.54 $\pm$ 0.39	2.98 $\pm$ 0.72	1.09 $\pm$ 0.22	0.70 $\pm$ 0.31
	(Min-Max)	0.41 – 0.82	4.94 – 6.11	2.22 – 4.09	0.76 – 1.33	0.44 – 1.16
Acy	Mean $\pm$ SD	0.47 $\pm$ 0.19	1.89 $\pm$ 0.22	1.18 $\pm$ 0.21	0.54 $\pm$ 0.12	0.52 $\pm$ 0.16
	(Min-Max)	0.31 – 0.74	1.55 – 2.20	0.87 – 1.42	0.42 – 0.72	0.39 – 0.75
Ace	Mean $\pm$ SD	0.38 $\pm$ 0.26	2.05 $\pm$ 0.42	0.92 $\pm$ 0.30	0.81 $\pm$ 0.03	0.46 $\pm$ 0.24
	(Min-Max)	0.20 – 0.74	1.54 – 2.62	0.60 – 1.33	0.77 – 0.84	0.29 – 0.81
Flu	Mean $\pm$ SD	0.39 $\pm$ 0.13	1.60 $\pm$ 0.26	0.65 $\pm$ 0.21	0.51 $\pm$ 0.22	0.40 $\pm$ 0.11
	(Min-Max)	0.27 – 0.59	1.25 – 1.94	0.48 – 0.95	0.30 – 0.81	0.28 – 0.57
Phe	Mean $\pm$ SD	0.53 $\pm$ 0.07	1.89 $\pm$ 0.25	0.98 $\pm$ 0.54	0.89 $\pm$ 0.25	0.66 $\pm$ 0.16
	(Min-Max)	0.43 – 0.62	1.57 – 2.25	0.57 – 1.76	0.63 – 1.21	0.51 – 0.90
Ant	Mean $\pm$ SD	0.22 $\pm$ 0.14	1.93 $\pm$ 1.23	0.79 $\pm$ 0.69	0.32 $\pm$ 0.24	0.28 $\pm$ 0.13
	(Min-Max)	0.12 – 0.42	0.33 – 3.19	0.31 – 1.79	0.15 – 0.66	0.18 – 0.47
Flt	Mean $\pm$ SD	0.31 $\pm$ 0.09	2.57 $\pm$ 0.38	2.24 $\pm$ 0.38	1.04 $\pm$ 0.23	0.88 $\pm$ 0.35
	(Min-Max)	0.21 – 0.44	2.04 – 3.04	1.76 – 2.76	0.83 – 1.40	0.60 – 1.40
Pyr	Mean $\pm$ SD	0.63 $\pm$ 0.06	1.14 $\pm$ 0.15	0.76 $\pm$ 0.06	0.73 $\pm$ 0.04	0.66 $\pm$ 0.06
	(Min-Max)	0.56 – 0.73	0.93 – 1.32	0.70 – 0.86	0.68 – 0.80	0.58 – 0.75
BaA	Mean $\pm$ SD	0.17 $\pm$ 0.05	0.72 $\pm$ 0.07	0.48 $\pm$ 0.03	0.30 $\pm$ 0.05	0.28 $\pm$ 0.07
	(Min-Max)	0.10 – 0.24	0.65 – 0.86	0.45 – 0.52	0.23 – 0.37	0.20 – 0.38
Chr	Mean $\pm$ SD	ND	0.92 $\pm$ 0.26	0.56 $\pm$ 0.26	0.45 $\pm$ 0.12	0.38 $\pm$ 0.10
	(Min-Max)		0.58 – 1.21	0.36 – 0.92	0.35 – 0.63	0.27 – 0.55
BbF	Mean $\pm$ SD	0.39 $\pm$ 0.24	1.88 $\pm$ 0.84	1.08 $\pm$ 0.57	0.71 $\pm$ 0.21	0.57 $\pm$ 0.40
	(Min-Max)	0.22 – 0.74	0.77 – 2.73	0.62 – 1.89	0.53 – 1.02	0.29 – 1.15
BkF	Mean $\pm$ SD	0.25 $\pm$ 0.11	1.25 $\pm$ 0.43	0.85 $\pm$ 0.34	0.51 $\pm$ 0.04	0.20 $\pm$ 0.16
	(Min-Max)	0.11 – 0.38	0.66 – 1.67	0.55 – 1.36	0.46 – 0.59	0.08 – 0.43
BaP	Mean $\pm$ SD	ND	0.21 $\pm$ 0.06	0.14 $\pm$ 0.03	0.10 $\pm$ 0.01	0.11 $\pm$ 0.002
	(Min-Max)		0.13 – 0.27	0.11 – 0.18	0.09 – 0.12	0.11 – 0.113
IcdP	Mean $\pm$ SD	0.17 $\pm$ 0.10	1.79 $\pm$ 0.13	1.74 $\pm$ 0.41	1.40 $\pm$ 0.89	1.22 $\pm$ 0.90
	(Min-Max)	0.03 – 0.27	1.61 – 1.98	1.21 – 2.34	0.22 – 2.27	0.03 – 2.00
DBA	Mean $\pm$ SD	0.43 $\pm$ 0.18	1.59 $\pm$ 0.19	1.51 $\pm$ 0.24	1.29 $\pm$ 0.32	1.03 $\pm$ 0.21
	(Min-Max)	0.25 – 0.61	1.31 – 1.75	1.18 – 1.75	0.84 – 1.63	0.75 – 1.32
BgHiP	Mean $\pm$ SD	ND	1.25 $\pm$ 0.09	1.01 $\pm$ 0.08	0.91 $\pm$ 0.07	0.86 $\pm$ 0.07
	(Min-Max)		1.10 – 1.39	0.91 – 1.12	0.79 – 1.00	0.76 – 0.95

**Note:** \*ND indicates concentrations below the analytical detection limit

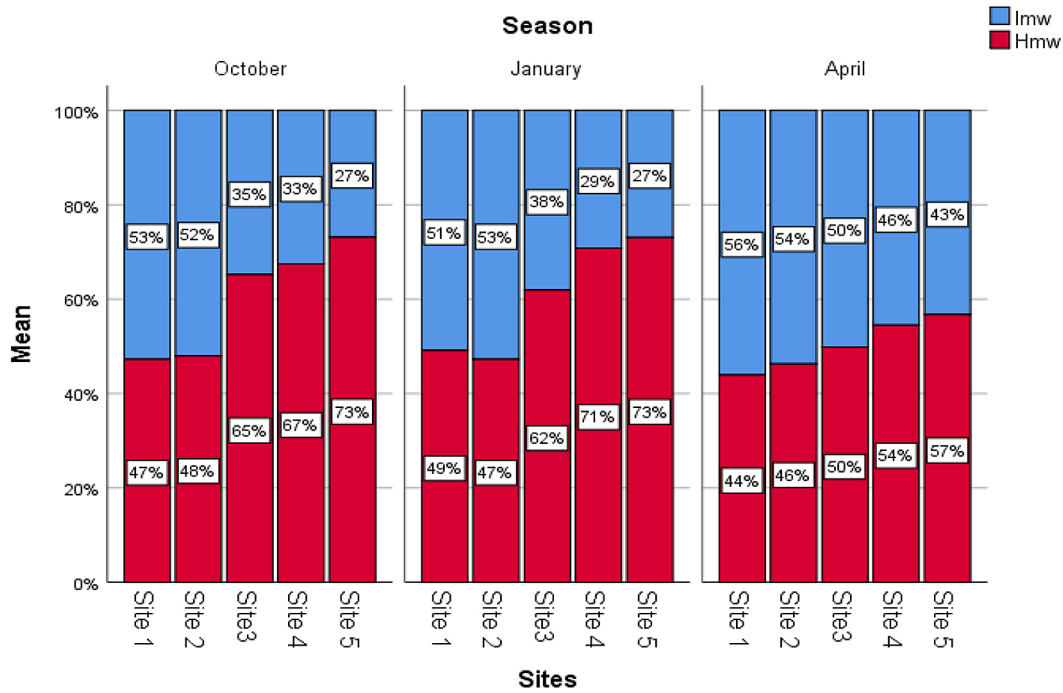
>0.55 indicates high-temperature sources (Wild et al., 1992; Cao et al., 2020). At S4 and S5, October ratios show BaA/(BaA + Chr) >0.35 (0.48–0.55) and IcdP/(IcdP + BghiP) >0.50, though Flu/(Flu + Pyr) remains petrogenic (0.33–0.37). January presents a similar mix, with Flu <0.40, indicating dilution of combustion residues. In April, IcdP collapses to 0.20 (S4) and 0.03 (S5), signaling a petroleum pulse, while Flu surges to 0.46–0.53 and BaA holds at 0.28–0.29, reflecting petroleum combustion. Overall, unburned oil inputs in spring partly mask but do not erase

the persistent pyrogenic signature exported from the Medical City outfall.

## Risk assessment

### Risk quotient

The Iraqi Quality Standards. take a minimalist approach as they bundle all dissolved and particulate hydrocarbons under a single blanket cap of 10  $\mu\text{g L}^{-1}$ .and only set an 0.7  $\mu\text{g L}^{-1}$  limit for Benzo[a]pyrene (COSQC, 2009). Most national frameworks still leave big holes. EPA's National



**Figure 2.** Percentage of LMW and HMW PAHs at the five sites during October, January, and April

**Table 4.** Characteristic diagnostic-ratio ranges for identifying PAH sources

Diagnostic ratio	Petrogenic	Fuel combustion	Pyrogenic and biomass burning
Ant / (Ant + Phe)	< 0.1	> 0.1	–
Flu / (Flu + Pyr)	< 0.4	0.4–0.5	> 0.5
BaA / (BaA + Chr)	< 0.2	> 0.35	0.2–0.35
IcdP / (IcdP + BghiP)	< 0.2	0.2–0.5	> 0.5

Recommended Water Quality Criteria publishes human-health thresholds for just 12 of the 16 priority PAHs (U.S. EPA, 2024). and Canada’s CCME freshwater guidelines cover only 9 of them (CCME, 1999). In contrast, the Dutch National Institute for Public Health and the Environment, in its 2012 Report, National Institute for Public Health and the Environment (RIVM) sets compartment-specific MPC values for all 16 congeners (RIVM, 2012), which are routinely used when a complete ecological benchmark set is needed. These values represent chronic effect thresholds below which no long-term adverse ecological effects are expected. The risk quotient (RQ) is a screening-level metric used to estimate the potential ecological risk of a contaminant. It is calculated as the ratio of the measured environmental concentration ( $MEC_i$ ) to the maximum permissible concentration ( $MPC_i$ ) for the same compound. Table 5 shows interpretation of risk quotient ( $RQ_i$ ) values.

For each compound and sample:

$$RQ_i = \frac{MEC_i}{MPC_i} \quad (1)$$

where:  $RQ_i$  – risk quotient for compound  $i$ ,  $MEC_i$  ( $\mu\text{g/L}$ ) – measured environmental concentration of compound  $i$  in surface water,  $MPC_i$  ( $\mu\text{g/L}$ ) – maximum permissible concentration established for compound  $i$ , representing the chronic no-effect level for aquatic organisms.

Risk-quotient analysis reveals a pervasive and severe mixture effect across the study area: the summed RQ ( $\Sigma RQ$ ) at every station consistently

**Table 5.** Interpretation of risk quotient values

$RQ < 1$	Low/no risk expected.
$RQ \geq 1$	Potential chronic risk to aquatic life
Higher RQ values	Urgent attention required

**Table 6.** Mean risk quotient and toxic-equivalency assessment of individual PAHs in Tigris River water

PAHs	TEF	MPC	Oct.			Jan.			Apr.		
			Mean MPC RQ	Mean TEQ ng/l	% $\Sigma$ TEQ	Mean MPC RQ	Mean TEQ ng/l	% $\Sigma$ TEQ	Mean MPC RQ	Mean TEQ ng/l	% $\Sigma$ TEQ
Nap	0.001	2	1.26	1.95	0.01	1.59	2	0.11	0.42	2.57	0.16
Acy	0.001	1.3	0.79	0.81	0.04	0.92	0.84	0.05	0.42	1.1	0.07
Ace	0.001	3.8	0.25	0.69	0.04	0.32	0.86	0.05	0.16	1.22	0.08
Flu	0.001	1.5	0.62	0.69	0.04	0.49	0.6	0.03	0.31	0.82	0.05
Phe	0.001	1.1	0.91	0.87	0.05	1.08	0.8	0.05	0.7	1.29	0.08
Ant	0.01	0.1	8.12	2.34	0.13	9.84	7.68	0.43	3.26	11.2	0.71
Flt	0.001	0.12	10.92	1.48	0.08	16.2	1.34	0.08	8.07	1.4	0.09
Pyr	0.001	0.023	35.83	0.77	0.04	36.43	0.79	0.04	30.17	0.79	0.05
BaA	0.1	0.012	33.33	42.6	2.29	41.17	37.6	2.12	23.17	37	2.36
Chr	0.01	0.07	4.43	4.17	0.22	9.29	5.02	0.28	5.97	8	0.51
BbF	0.1	1.3	54.35	53.2	2.86	70.82	88.4	4.99	38.71	137	8.72
BkF	0.1	0.93	33.53	45.6	2.45	55.76	53.8	3.04	18.35	83.6	5.32
BaP	1	0.01	8	112.7	6.06	14.8	162.3	9.16	8.6	159.5	10.15
IcdP	0.1	0.0027	311.1	167.8	9.02	665	147.4	8.32	424.4	79	5.03
DBA	1	0.0014	560	1415	76.08	1088	1252	70.68	794.2	1036	65.95
BghiP	0.01	0.0082	58.78	9.95	0.53	130.4	9.87	0.56	105.6	10.4	0.66

exceeds 100. Even the upstream reference site S1, fails to meet ecological safety, recording  $RQ > 1$  for seven to ten individual PAHs in each sampling period. Spatial patterns implicate the wastewater outfall at S2 as the principal point source; this station displays the highest single compound and cumulative RQs, and critically elevated risk persists for more than 1500 m downstream. The toxicity profile is dominated by HMW, carcinogenic PAHs particularly (DBA), (IcdP), (BbF).

#### *Benzo[a]pyrene-equivalent (TEQ) assessment*

This approach quantifies the overall carcinogenic potency of the PAH mixture by converting each of the 16 measured congeners into a benzo[a]pyrene-equivalent concentration (TEQ). Concentrations of the 16 EPA-priority PAHs were multiplied by the toxic-equivalency factors (TEFs) (ATSDR, 2022). Summing the 16 products yielded a benzo[a]pyrene-equivalent concentration ( $\Sigma$ TEQ) for every sample. Seasonal means were obtained by averaging the five station values within each campaign (October 2024, January 2025 and April 2025) and are reported in Table 6. Across the three surveys, cumulative  $\Sigma$ TEQ peaked in October at  $1.86 \mu\text{g BaP eq L}^{-1}$ , declined slightly to  $1.77 \mu\text{g BaP eq L}^{-1}$  in January ( $-4.8\%$ ), and reached a minimum of  $1.57 \mu\text{g BaP eq L}^{-1}$  in April ( $15.6\%$ ). In

every season, the toxicity profile was dominated by high-molecular-weight congeners: DBA alone contributed 66–76% of  $\Sigma$ TEQ and posted mean risk quotients (RQs) of 560–1089, two to three orders of magnitude above its maximum permissible concentration. IcdP added a further 8–9% (RQs 311–666), while benzo[b] and benzo[k]fluoranthene together accounted for 5–9. LMW PAHs each contributed  $\leq 0.2\%$  of  $\Sigma$ TEQ despite forming up to 10% of the mass load. The slight winter rise in (IcdP) toxicity and the progressive decline in DBA's fractional dominance toward spring suggest an interplay of reduced photolysis with higher organic inputs during colder months and enhanced dilution or degradation later in the year. Overall, a handful of 4–6-rings PAHs drive more than 90% of the mixture's toxic potency, marking them as priority targets for future mitigation and monitoring efforts along the Tigris River.

## CONCLUSIONS

This study provides a comprehensive assessment of (PAHs) contamination in the Tigris River near Baghdad Medical City across three seasonal seasons. The findings reveal that PAH concentrations at the discharge point and



downstream stations consistently exceed ecological and human health safety thresholds, particularly during October. The diagnostic ratios point to a dominant pyrogenic origin of contamination, while risk quotient and toxic equivalency evaluations highlight a persistent and serious ecological threat. These results underscore the urgent need for regulatory intervention, improved wastewater treatment, and continuous environmental monitoring in urban rivers impacted by hospital effluents.

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