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Polycyclic aromatic hydrocarbons in the surface water and sediment along Euphrates River system: Occurrence, sources, ecological and health risk assessment

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ABSTRACT

This study presented for the first time a comprehensive measurement campaign of 16 PAHs along the Euphrates River for five months, in both water and sediment samples. Our study revealed that the PAHs contamination increased along the flow direction due to the increasing non-point pollution and the return flows of agriculture. The 5–6 rings PAHs were dominant in water and sediment samples with an average of 42 % and 50 %, respectively. The diagnostic ratios of PAHs suggest that the pollution of these compounds originated mainly from petroleum product combustions. The carcinogenic PAHs formed 46 % and 55 % of the total measured compounds in water and sediment samples, respectively, which highlights potential ecological and human health risks. Based on sediment quality guidelines (SQGs), most sites exhibit an effect range between low and medium. The calculated incremental lifetime cancer risk (ILCR) for adult and children were in the 10^{-2} – 10^{-3} range, which is 3–6-fold higher than what was reported in the literature. These observations call for urgent attention from environmental authorities of countries sharing this key water source in Western Asia.

1. Introduction

Environmental concerns have always been of outstanding importance to humanity (Wang and Yang, 2016). Rivers host various micro- and macro-organisms that are threatened by pollution. Organic and inorganic pollutants enter river basins with polluted wastewater, effluent discharge, stormwater runoff and air deposition (Abdel-Shafy and Mansour, 2016; Sabater and Elosegi, 2014; Lee et al., 2020). Toxic contaminants can be accumulated in aquatic species such as fish and mussels; since they serve as food, they can constitute a significant health risk to humans (Lee et al., 2015, 2020; Tongo et al., 2017). River

sediments are significant sinks for several pollutants, and sediment resuspension releases toxins back into the water body (Lee et al., 2013, 2020; Salomons and Brils, 2004). Diverse contaminants in the sediment similarly maintain a dynamic equilibrium of adsorption and emission with the overlying water (Zhu et al., 2013; Hill et al., 2013). When the physical and chemical properties of the water-sediment interface change via diffusion, desorption, disturbance, etc., pollutants may be re-released into the overlying water, and the sediments transform from being a “sink” to a “source” of contaminants. Given the possible dangers posed by polluted sediment through chemical and biological interactions with the overlying water body, it is crucial to collect data on

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sediment quality and ecological risk conditions (Wang et al., 2020; Armid et al., 2014). To preserve and restore the good ecological status of aquatic ecosystems and to protect human health, it is essential to have a deeper understanding of the distribution and the risk level of pollutants in river ecosystems (Sabater and Elosegi, 2014). Therefore, intense monitoring and assessment of the water are urgently needed (Hernandez-Ramirez et al., 2019).

Polycyclic aromatic hydrocarbons (PAHs) are a class of concerning contaminants that can cause a severe threat to human health and cause direct or indirect harm to aquatic organisms and ecosystems (Xu et al., 2021). PAHs have taken considerable attention due to their ecological danger, socioeconomic repercussions, and impact on human health (Grice et al., 2017; Zhao et al., 2014; Mitra et al., 2019). The main anthropogenic sources of PAHs are industrial activities, combustion of fossil fuels and waste, automobile exhausts, and even natural sources, like forest fires and volcanic eruptions (CCME (Canadian Council of Ministers of the Environment), 1999; Abdel-Shafy and Mansour, 2016). PAHs are a large group of persistent, toxic, genotoxic, and carcinogenic environmental contaminants (Shen et al., 2013; Han and Currell, 2017). Based on their characteristics and molecular weights, PAHs can be divided into two categories which are low molecular weight (LMW) compounds with two or three benzenoid rings that typically predominate in the water body and high molecular weight (HMW) compounds with four to six benzenoid rings that are prevailing in sediments medium (Zeng et al., 2018). Due to their potential mutagenicity, toxicity, and/or carcinogenicity to humans' health, several PAHs are categorized as priority pollutants (USEPA, 2014; Zelinkova and Wenzl, 2015). Based on their thermodynamic characteristics, PAHs are categorized into three types. The first one is pyrogenic, which comes from the incomplete combustion/pyrolysis of organic substances, such as fossil fuels, biomass, tobacco, garbage, and charbroiled meat. The second type is called petrogenic, which releases from the use of crude oil and related products and oil spills. The third type is biogenic/diagenetic, which is produced by the slow transformation of organic matter in sediments (Abdel-Shafy and Mansour, 2016; ATSDR (Agency for Toxic Substances and Disease Registry), 1995; Kanzari et al., 2012).

PAHs are derived from the incomplete combustion of organic materials such as tobacco, fossil fuels, wood, and petroleum products, and they are pervasive contaminants and important parts of air pollution. For example, our team has found a considerable amount of PAHs in street dust in Iraq (Grmasha et al., 2022). Increasing the number of automobiles in Iraq elevates the PAHs concentration in the atmosphere as well. Moreover, regular gas and fuel combustion activities in most Iraqi provinces can generate a considerable amount of PAHs. The presence of gasoline and diesel-powered generators in most urban areas could be another significant source of PAHs pollution (Hamad et al., 2015; Grmasha et al., 2022). In addition to all mentioned common PAHs sources in Iraq, the country is the fifth most vulnerable country to climate change in which the winter season is currently shrinking with exceptionally low precipitation (O'Driscoll and Fazil, 2022). This megadrought, because of increasing the summer months accompanied by high temperatures ($> 50\text{ }^{\circ}\text{C}$) leads to a reduction in water level. Therefore, there is a pressing urgency to develop conservation strategies for water sources, for which extensive water chemical, biological and hydrological survey and monitoring programs are required, similar to other international programs such as The European Water Framework Directive (WFD). This could help in identifying the pollution sources and devising effective mitigation plans.

A study on PAHs level water and sediment in Al-Hussainya River in Karbala Province was examined by Hassan et al. (2019). It showed that the total PAHs in water ranged from 0.24 to 58.72 ng/L and from 0.36 to 119.06 $\mu\text{g/g}$ dw for the sediment. Although the work referred in its title to the Euphrates River, it investigated only the Al-Hussainya River which is considered an estuary for the river. Another attempt to measure the PAHs load in sediment in the main Euphrates River from Al-Hindiya Barrageto Al- Kifil City in 2005–2006. The study found that the mean

value of total PAHs was 167 ng/g dw (Mohammed et al., 2009). Based on these studies and with the increase in the pollution sources in Iraq without any actual mitigation strategies, there is a need for comprehensive measurements for 16 PAHs along the Euphrates River and to fill knowledge gaps about the pollution level of one of the biggest and historically, most important rivers of Western Asia and provide a scientific basis for the development of effective water management strategies. Therefore, this work is dedicated to investigating (1) 16 PAHs, which are priority pollutants and potential carcinogens (Rengarajan et al., 2015; EPA, 2014), both in water and sediment samples along the main body of the river in Iraq, (2) to assess the ecological risk of these PAHs, (3) to analyze the composition profiles of PAHs in the river basins, (4) to determine the contribution rate of various sources of pollution, and (5) to assess the potential risks of PAHs pollution.

2. Materials and methods

2.1. Sampling sites

The Euphrates River, with a catchment area of 440,000 km^2 and a length of 2786 km, is the longest-running water in Western Asia. The source of the Euphrates River is in Turkey, runs through Syria, and its main inflows, with the Tigris River in Iraq to create the Shatt al Arab, which flows into its final erosion base, the Persian Gulf. The estimated population of the Euphrates Basin is around 23 million, with 44 % residing in Iraq, 31 % in Turkey and 25 % in Syria. In the catchment area of the river, Euphrates irrigation, hydropower, and drinking water supply are the primary uses of water. Agriculture utilizes most of the water ($>70\%$). This highlights the significant importance of the river in the agriculture and energy sector of the countries sharing its basin, especially Iraq, with its highest population number. The return flows from agricultural drainage produce secondary salinization (particularly in the Iraqi region) along the river's course. Moreover, the discharge of untreated sewage leads to further deterioration of water quality in the river (UN-ESCWA and BGR (United Nations Economic and Social Commission for Western Asia and Bundesanstalt für Geowissenschaften und Rohstoffe), 2013). Thus, thirteen sampling sites of the Euphrates River were investigated in Iraq, namely Haditha (S1), Hit (S2), Ramadi (S3), Al-Fallujah (S4), Jorf Al-Sakhar (S5), Musayyib (S6), Hindiyah (S7), Kefel (S8), Najaf (S9), Al-Qadisiyyah (S10), Samawah (S11), Nasiriyah (S12), and Basrah (S13) (Fig. 1). The coordinated sampling sites are presented in the supplementary materials (Table S1).

2.2. Reagents and chemicals

All solvents, including methanol, methylene chloride, hexane, ethyl acetate and acetone were HPLC-grade and acquired from Fisher Chemical Co. (United States), with a minimum of 99 % purity. The reference standards of the 16 PAHs (QTM PAH-Mix, 2000 $\mu\text{g/mL}$), including naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenz[a,h]anthracene (DahA), benzo[g,h,i] perylene (BghiP), and Indeno(1,2,3-cd)pyrene (IND) were bought from Supelco (Bellefonte, PA, USA). Solid-phase extraction membranes (ENVITM-18 DSK SPE Disk, diam. 47 mm), Silica gel (desiccant $\sim 2\text{--}5$ mm), Sodium Sulfate Anhydrous and PAH recovery standards were obtained from Sigma-Aldrich, USA. Silica gel and Sodium Sulfate Anhydrous were placed in a furnace oven (FI 600–60, Borel) at $500\text{ }^{\circ}\text{C}$ for four hours to eliminate organics or moisture, then stored in a sealed desiccator until use. In the experiments, a Milli-Q system with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ ($25\text{ }^{\circ}\text{C}$) and a TOC value <5 ppb was used. Ultrasonic cleaners (HeidolphTM, Fisher Scientific) were first used to clean glassware, which was subsequently washed with acetone and hexane.

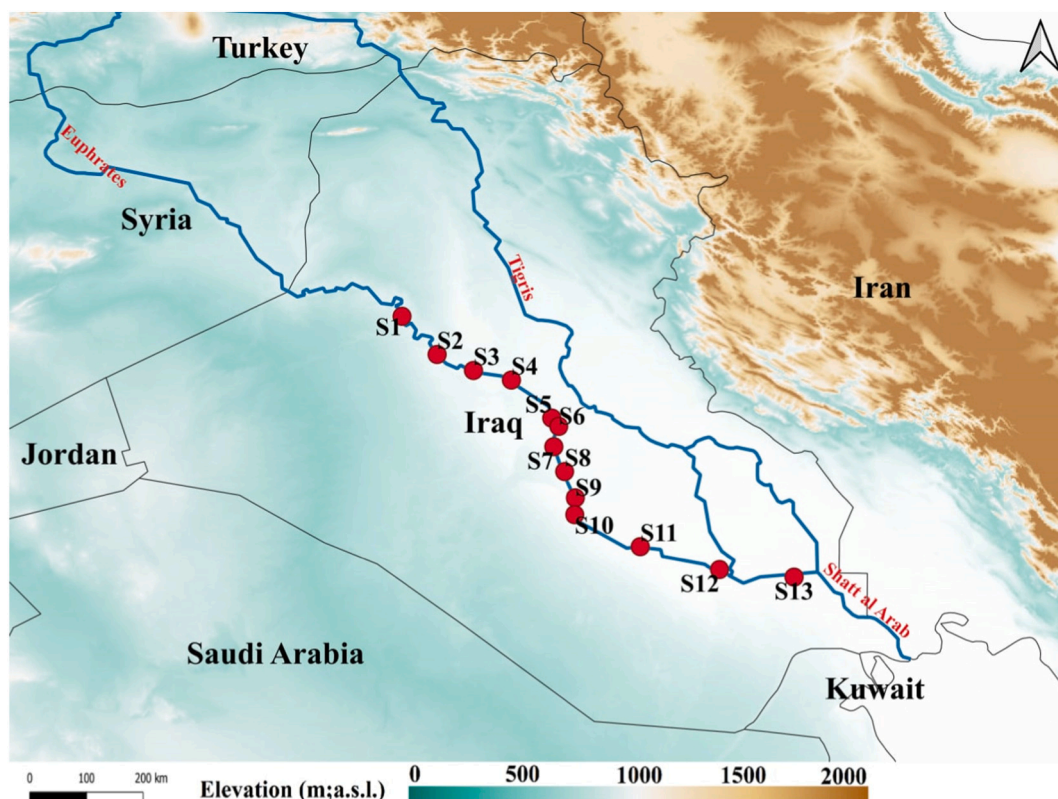


Fig. 1. Sampling locations along the Euphrates River in Iraq.

2.3. Collection and analysis

Both surface water and sediment samples were carried out from March 2022 to July 2022, monthly. Each site was measured five times during this period. All surface water samples were collected from 10 to 30 cm below the water's surface using a pre-cleaned stainless-steel container. Each water sample was spiked with 1 µg of fluoranthene-d10, the PAH recovery standard, and they were sealed in 6 L glass containers, returned to the laboratory within a day, and kept at 4 °C until the analysis. In order to separate PAHs for analysis, 6 L of surface water was filtered through a glass fiber membrane of 0.45 µm and then a methanol-activated solid-phase extraction membrane (SPE) to isolate PAHs. According to the procedure reported by (Lin et al., 2018), the SPE containing PAHs was subsequently wrapped in foil and cooled for further analysis. Using a pre-cleaned grab sampler, sediment samples were collected and kept in sealed bags. At the same site, sediment samples (0–10 cm) were collected three times using a grab sampler, then blended and preserved in dark glass bottles. After collection, samples were directly delivered to the laboratory for further analyses.

The PAHs extraction from the SPE membrane was based on the previously reported procedure (Lin et al., 2018; TERNON and Tolosa, 2015): the dichloromethane-ethyl acetate and ethyl acetate solutions were used to elute the SPE extraction membrane twice. Afterwards, the extracts were combined, dried over anhydrous sodium sulfate, concentrated using a rotary evaporator, and then redissolved in one milliliter of n-hexane.

In order to extract the sediments, approximately two g of the dry-freeze sample were precisely weighed after sieved with 100 stainless steel mesh spiked with 1 µg of fluoranthene-d10 and transferred to an extract tube containing 25 mL of acetone-hexane (1:1), extracted using a microwave digestion system. The temperature was increased from 25 to 120 °C at 8 °C/min and kept for 20 min. Then, samples were centrifuged at 2000 rpm for 20 min. The supernatants were processed through anhydrous sodium sulfate and then extracted and purified using a glass

chromatography column. The final samples were evaporated to reach a volume of around 2 mL, and then 1 mL of n-hexane for measurement was added.

The PAHs measurements were accomplished via utilizing a gas chromatography–mass spectrometry (GC–MS, Agilent 6890 N 5975C mass selective detector, USA) as reported in our previous work (Grmasha et al., 2022). Helium was used as a carrier gas for GC–MS analysis at 1.5 mL/min with an HP-5MS gas chromatography column (30 m × 0.32 mm × 0.25 µm). The injector temperature was set at 300 °C, and selective ion scanning (SIM) mode was used for quantitative analysis. The oven temperature was programmed as follows: the initial temperature started at 100 °C for 1 min and then increased to 300 °C at a rate of 8 °C/min and was held at 300 °C for 39 min. Blanks and reference samples were measured to check for analysis accuracy. In addition, triplicate runs for each sample were measured, which in turn made the relative standard deviation of <6 %.

2.4. Quality control and measurements

Prior to each experiment, glassware was heated to 150 °C and rinsed with methanol, acetone, and dichloromethane to reduce background contamination. External standard methods were used to determine the quantitative standards for PAHs in the water sample. For 16 PAH monomers, the linearity correlation values ranged between 0.998 and 0.999. The PAHs concentrations in the sediment samples were determined as dry weight. The limits of detection (LOD) were determined from the analyte concentration and obtained using a 3-fold signal-to-noise ratio (Zhu et al., 2015). The LOD for water samples ranged from 0.04 to 0.28 ng/L, whereas the LOD for sediment samples was 0.09 to 0.65 ng/g, dry weight (dw).

In order to conduct recovery experiments, 16 PAHs standard solutions were spiked into the water and sediment samples following the procedure reported by (Dong et al., 2022; Lin et al., 2018; Zhu et al., 2015; Wang et al., 2015). The recovery ranges of 16 PAHs samples were

90.4 %-100 % and 81.4 %-97.6 % for water and sediment samples, respectively. The recovery ranges of the spiking standards (surrogate, fluoranthene-d10) were 92.6 %-106.8 % for water samples and 85.4 %-95.3 % for sediment samples (Table S2). The PAH concentrations were recovery corrected. Water and sediment samples were measured in triplicate, and the results are presented in mean values. All the data in this work has been subjected to a normality test by the Kolmogorov-Smirnov method with a significance level of 0.05.

3. Results and discussion

3.1. PAHs concentrations in water

The spatial and temporal variation of PAHs concentration in water samples is shown in Fig. 2. Fig. 2 reveals that in March, the water samples from S11 and S13 had the highest 16 PAHs. According to April measurements, S11 remained the highest, followed by S12 and S13. In May and July, however, the 16 PAHs were highest in S12, followed by S13. Finally, June measurements revealed that S11, S13, and S12 had the highest concentrations of 16 PAHs. The downstream locations S11, S12, and S13 have the highest PAH concentrations compared to other sites along the main river body. An illustration of this variation along the river course is illustrated in Fig. S1 to provide a summary of PAHs distribution. The spatial variation of PAHs is clear since the concentration of the different PAHs unequivocally increases from upstream to downstream. However, Fig. 2 shows no clear trends in the temporal variation of the PAHs concentration in the water samples. Several factors make it harder to understand the PAHs variation in the Euphrates River, such as the irregular discharge of wastewater, the various activities of different industries (e.g., oil and agriculture), climate change impact on the seasonal shift in Iraq, the complex geology of the river and the various activities of different industries (e.g., oil and agriculture) in the surrounding area of the river.

3.2. PAHs concentrations in sediment

The spatial and temporal variation of PAHs concentration in water and sediment samples is shown in Fig. 3. An illustration of this variation along the river course is provided in Fig. S2 to provide a summary of PAHs distribution. Fig. 3 demonstrates that in March, S5, S12, and S4 sediment samples had the highest levels of 16 PAHs. Site 5 remained the highest according to April measurements, followed by S12 and S8. In May, however, S12 had the highest levels of the 16 PAHs, followed by S11. Measuring conducted in June found that S12, S13, and S5 had the highest values of 16 PAHs. Last month, S5 and S12 contained the highest 16 PAHs. Both S5 and S12 had the highest concentrations of the 16 PAHs in the sediment along the main river body. The spatial variation of PAHs is clear since the concentration of the different PAHs unequivocally increases from upstream to downstream. However, Fig. 3 shows no clear trends in the temporal variation of the PAHs concentration in the water and sediment samples. A similar outcome was reported by Duodu et al. (2017), who also found it hard to form any conclusion regarding the temporal variation of PAHs measured in different months around the year due to the observed weak correlations between PAHs compounds. There is a number of factors that make it harder to understand the spatial and temporal variation of PAHs in the Euphrates River, such as the irregular discharge of wastewater, the various activities of different industries (e.g., oil and agriculture), the complex geology of the river and the various activities of different industries (e.g., oil and agriculture) in the surrounding area of the river. Furthermore, climate change is undoubtedly one of Iraq's most serious challenges among MENA countries, having significant negative effects on the environment, water resources, and economy, especially the agricultural sector (Namdar et al., 2021). The reduced river flow has affected the water bodies, mostly due to the dams erected on the major rivers and occasionally to drought (Moridnejad et al., 2015). These factors lead to accumulating amount of

sediment along the entire waterbody, which in turn could increase the level of PAHs.

3.3. Overall PAHs concentrations in water and sediment along the Euphrates basin

Fig. 4 displays the results of the mean concentrations of 16 PAHs detected in water (A) and sediment (B) samples. It can generally be seen that all the targeted PAHs were detected in all locations along the river, which ranged from 464 to 992 ng/L and 5940 to 9723.9 ng/g dw for water and sediment, respectively. The IND has the highest average concentration both in water (65.22 ng/L) and sediment (863.30 ng/g dw) samples, and this account for almost 9 % and 11 %, respectively, of the \sum 16 PAHs. The least average concentration among all the PAHs was recorded for Fl (34.30 ng/L) in water samples and Nap (247.34 ng/g dw) in sediment samples. It is also clear that location 2 (Hit) had the lowest \sum 16 PAHs in both water (464.00 ng/L) and sediment (5940.00 ng/g dw) samples. Location 13 had the highest \sum 16 PAHs in water samples (991.85 ng/L), whereas location 12 had the highest \sum 16 PAHs in sediment samples (9723.9 ng/g dw). It can be noticed that the \sum 16 PAHs in the upper stream was less than in the lower stream locations. This could be explained by introducing several (point and non-point) sources of pollution, such as direct wastewater disposal and dust, which increases the level of PAHs in the water system (Al Bomola, 2011; Grmasha et al., 2022).

The range of \sum 16 PAHs in the Euphrates water (464–992 ng/L) is higher than those in the Yellow River Delta (64.8–335 ng/L) (Wang et al., 2009) in China, the Shanghai River (46.53–222 ng/L) (Liu et al., 2016), the Soan River (61–207 ng/L) in Pakistan (Aziz et al., 2014) and in surface waters of the Gulf of Gabes (17.6–71.2 ng/L) Southern Mediterranean Sea, Tunisia (Zaghden et al., 2022). It is also higher than the measured PAHs in harbours of the West coastal of the Gulf of Tunis in Tunisia in the summer (378.4 ng/L) and within the measurements during the winter season (703.1 ng/L) (Mzoughi and Chouba, 2011). The PAHs load of the water sample in this study was also higher than Al-Hussainya River (one of the Euphrates River estuaries), which ranged from 0.24 to 58.72 ng/L (Hassan et al., 2019). Nonetheless, it is lower than those in the Cauca River (52.1–22,888 ng/L) in Colombia (Sarría-Villa et al., 2016) and the Daliao River (71.12–4255 ng/L) in China (Zheng et al., 2016).

The PAHs concentrations in the sediment samples range from 5940 ng/g to 9723.9 ng/g dw with a mean value of 7762.7 ng/g dw. The maximum PAHs contamination level of drinking water as set by WHO is 200 ng/L (Ekanem et al., 2019; Ekere et al., 2019; WHO, 1998). This means that an effective removal method is required to decrease PAHs to the permissible level when using the river for drinking water production, especially in the downstream region when their concentrations reach the peak. Moreover, seven commonly studied PAHs are classified as carcinogenic compounds by the US Environmental Protection Agency (USEPA) like Chr, BbF, BkF, BaA, BaP, IND, and DBA. The contribution of these carcinogenic compounds to the \sum 16 PAHs in the water sample was about 46 %. This is much higher than the carcinogenic portion of the PAHs reported in seven major Chinese rivers, which was in the range of 3.5 %–28 % (Yu et al., 2021). Among the seven carcinogenic PAHs, BaP is widely discussed as the most potentially carcinogenic PAHs, and WHO set a maximum allowable limit for it in drinking water of 100 ng/L (Ekere et al., 2019). The BaP concentration in the Euphrates River, varying between 9.918 and 85.54 ng/L (mean = 50.02 ng/L) was lower than the WHO limit. However, it is higher than the limit set by the Canadian drinking water quality guideline of 40 ng/L in the sampling sites (Health Canada, 2019). For instance, S4 – S13 exceeded the presumable limit, whereas S1–S3 were below the Canadian water quality guideline. This again emphasizes the concerning health risks associated with using the river for fishing or water production, as these compounds could effectively transport the human body through ingestion (WHO, 2000).

The European Water Framework Directive (WFD) intends to attain

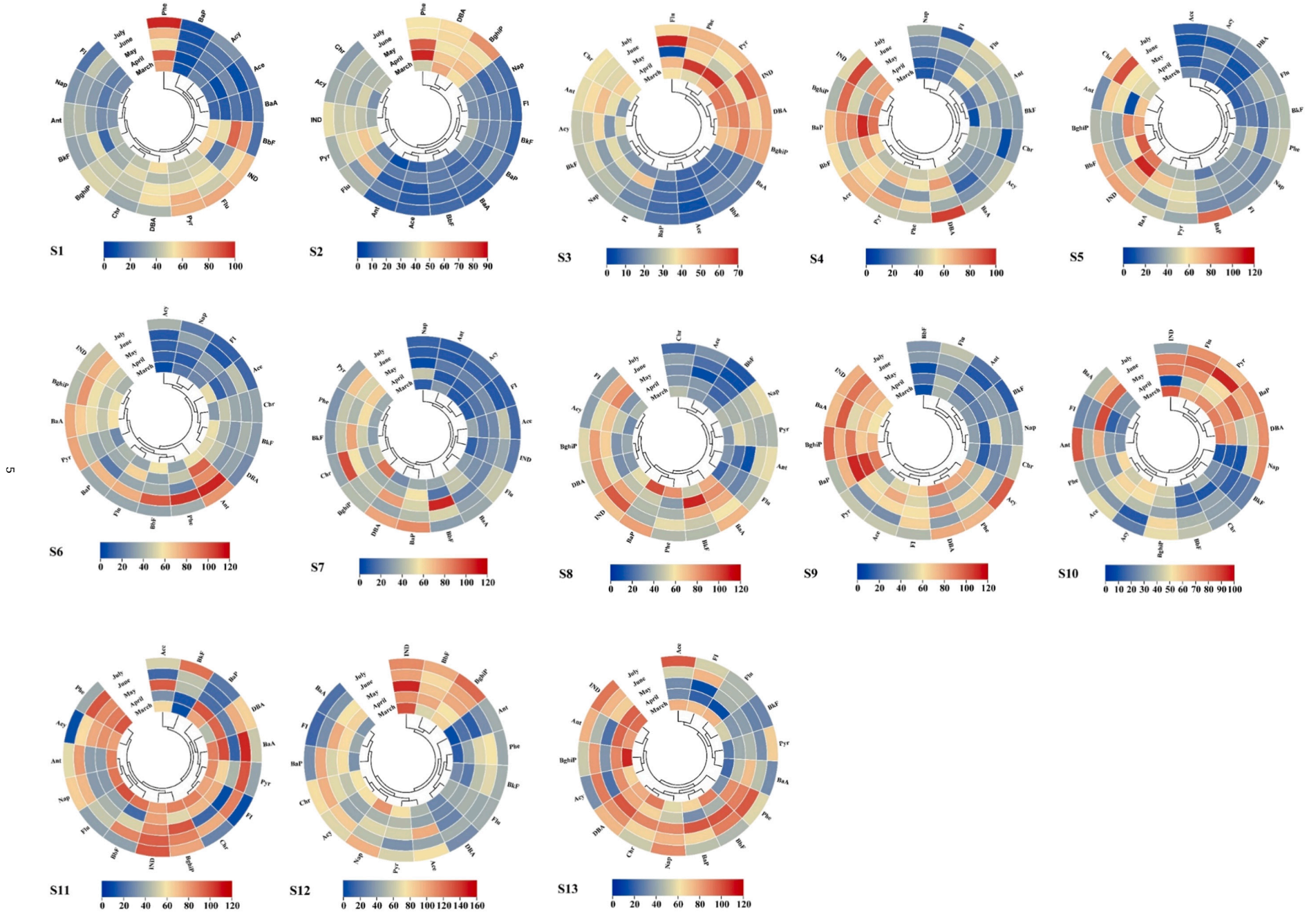


Fig. 2. PAHs concentrations in water samples. The scale bar represents PAHs concentration range (ng/L).

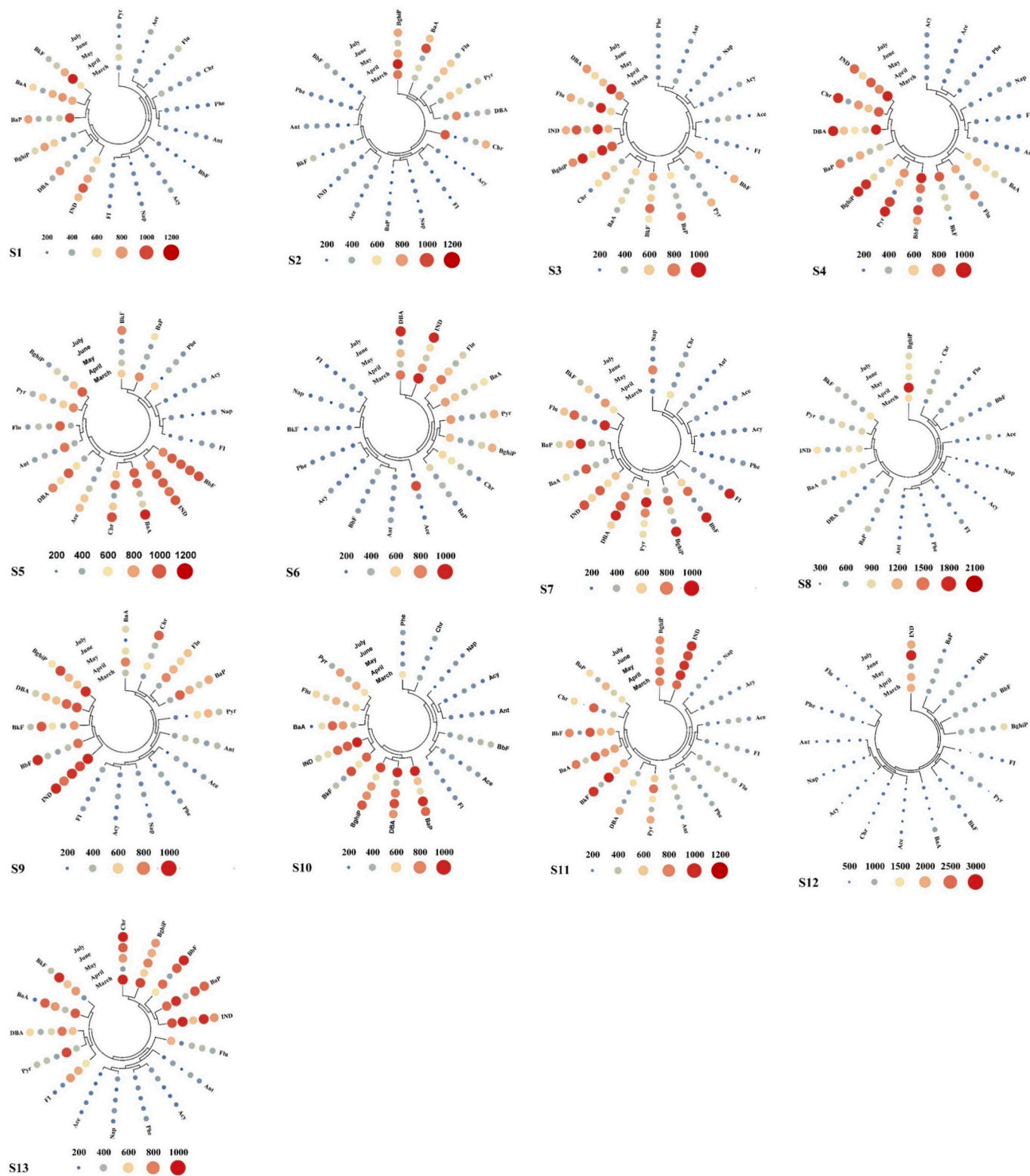


Fig. 3. PAHs concentrations in sediment samples. The bubble bar represents PAHs concentration range (ng/g dw).

and maintain “good status”, which should be the combination of “good chemical” and “good ecological” status (WFD, 2000; Jones et al., 2011). It mandates that EU Member States assess, monitor, and manage a variety of Priority Substances (PS) in all inland and coastal waterways. To protect human life and the environment, Environmental Quality Standards (EQS) were developed for every PS level that must not be exceeded. The vast majority of the PS consists of polar chemical compounds,

including eight PAHs: naphthalene, anthracene, fluoranthene, benzo[b]-fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene. Applying WFD to the water samples, it can be confirmed that Nap, Ant and Flu were below the limit in all sites, while BbF, BkF, BghiP and IND exceeded the allowable values in all sites. Additionally, BaP exhibited concentration above the limits in sites S4, S7-S10, S12 and S13, while others were below the allowable limits.

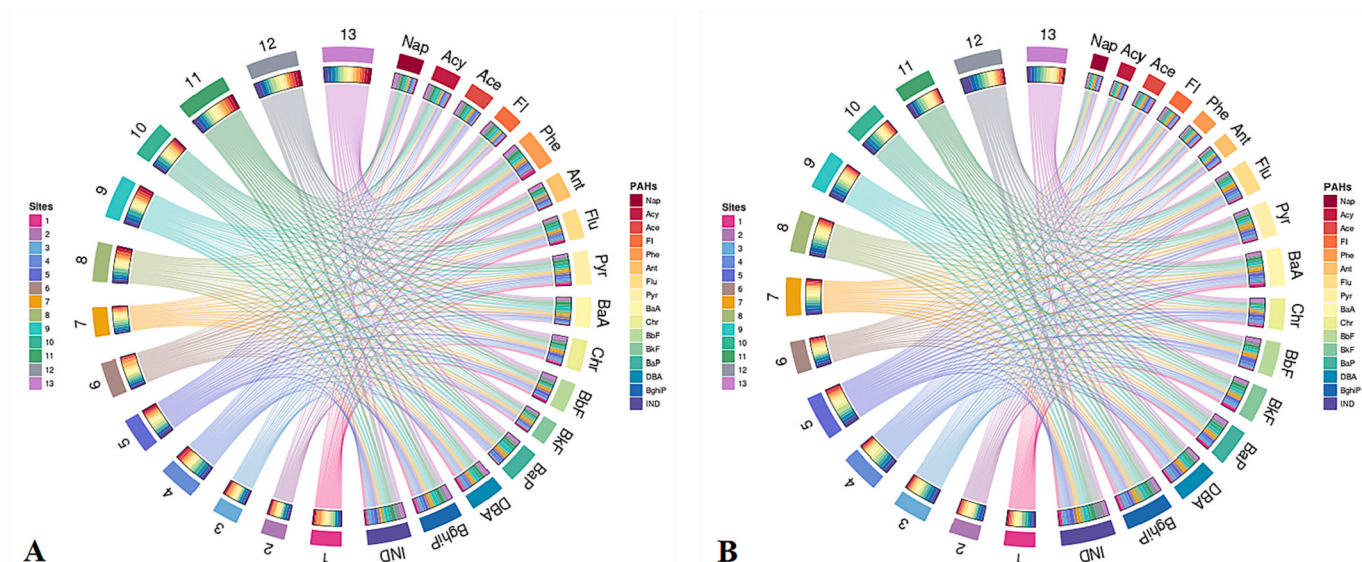


Fig. 4. PAHs mean concentrations measured in (A) water samples (ng/L) and (B) sediment samples (ng/g dw) of all the sampling sites.

The sedimentary \sum 16 PAHs measured in this study (5940–9724 ng/g dw) are higher than some of the reported literature, such as Brisbane River, Australia (148–3079 ng/g dw) (Duodu et al., 2017), River in Chongqing, China (221–3205 ng/g dw) (Lei et al., 2019), Rizhao coastal area, China (79.3–853 ng/g dw) (Chen et al., 2012), harbours of the West coastal of the Gulf of Tunis in Tunisia 1294.6 ng/g dw (Mzoughi and Chouba, 2011), Bizerte Lagoon, Tunisia (83.3–447.08 ng/g dw) (Trabelsi and Driss, 2005; Barhoumi et al., 2014) and Ghar El Melh Lagoon, Tunisia (39.59 to 655.28 ng/g dw) (Ameur et al., 2010). The PAHs level in the sediment is also higher than the measured load within the same river in 2005–2006 with total PAHs was 167 ng/g dw (Mohammed et al., 2009).

The PAHs load in the sediment is lower than the total PAHs in Al-Hussainya River (one of the Euphrates River estuaries in Karbala Province that ranged from 0.36 to 119.06 μ g/g dw. However, it was confusing to allocate the correct PAHs range in this study as in the abstract, it was in μ g/g dw, whereas in the Table it was ng/g (Hassan et al., 2019). Globally, the sedimentary PAHs concentrations were lower than those found in Athabasca Lake, Canada (10.6–130,180 ng/g dw) (Evans

et al., 2016), Huai River, China (810–28,228 ng/g dw) (Zhang et al., 2017) and coastal areas in Bangladesh (200–17,089 ng/g dw) (Habibullah-Al-Mamun et al., 2019). The carcinogenic species accounted for approximately 55 % of the \sum 16 PAHs. This exceeds the contribution of carcinogenic PAHs reported for the Brisbane River in Australia (46 %) (Duodu et al., 2017) and the Gao-ping River in Taiwan (22 %) (Doong and Lin, 2004). Although the later study was conducted 18 years ago, the PAHs levels might have changed significantly. Baumard et al. (1998) classified PAH concentrations in sediment as low (0–100 ng/g), moderate (100–1000 ng/g), high (1001–5000 ng/g), and very contaminated (>5000 ng/g). Based on the classification of Baumard et al. (1998) the Euphrates sediments are highly contaminated and require special attention from local authorities to mitigate such elevated concentrations.

3.4. PAHs composition in water and sediment

The PAHs measured in this study were divided into three groups based on the number of rings in their structure: 2–3 rings (low molecular

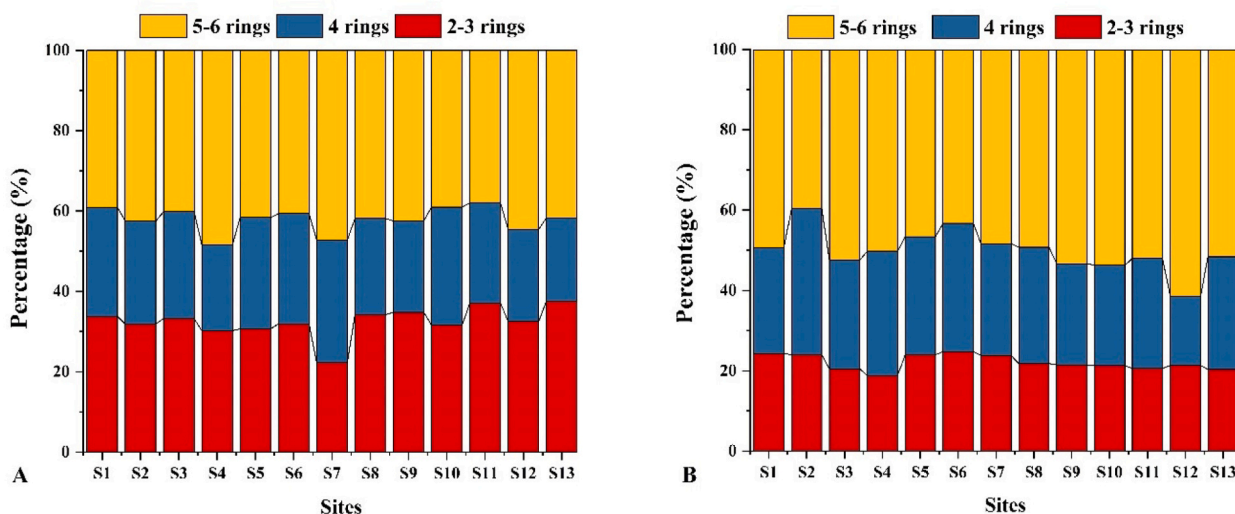


Fig. 5. Percentage distribution of PAHs based on the number of rings for (A) water samples and (B) sediment samples.

weight, LMW), 4 rings and 5–6 rings (high molecular weight, HMW). The percentage contribution of each of these groups to the ΣPAHs in water and sediment samples is presented in Fig. 5. Fig. S3 shows Ternary plots for water (A) and sediment samples (B).

The Euphrates water samples were mainly composed of 5–6 rings PAHs, accounting for 37.9(S11) to 48.3 % (S4) of ΣPAHs (average of 42 %), followed by 2–3 rings PAHs, accounting for 22.2 % (S7) to 37.6 % (S13) of ΣPAHs (average of 32 %). The 4 rings PAHs accounted for 20.7 % (S13) to 30.4 % (S7) of ΣPAHs (average of 26 %). The case is slightly different for the sediment samples.

The PAHs in Euphrates sediment samples mainly consisted of 5–6 rings PAHs, accounting for 40 % (S2) to 62 % (S12) of ΣPAHs (average of 50 %), followed by 4 rings PAHs, accounting for 17.1 % (S12) to 36.4 % (S2) of ΣPAHs (average of 28 %). The 2–3 rings PAHs accounted for 18.8 % (S4) to 24.7 % (S6) of ΣPAHs (average of 22 %). Similar observations were reported in previous studies (Lee et al., 2021; Liu et al., 2016; Li et al., 2010). The high percentage of HMW in sediments can be due to the low solubility of this fraction that led to its accumulation in sediments. The PAHs distribution in the Euphrates River was similar to 9 of the 30 rivers monitored in Taiwan (Lee et al., 2021). One of the seven rivers evaluated for PAHs in China also had similar ring distribution as the Euphrates River (Yu et al., 2021). The HMW PAHs are more resistant to degradation and might thus be transported and deposited in sediments more efficiently. In contrast, low-molecular-weight PAHs have greater water solubility and benthic recycling, resulting in their predominance in the dissolved aqueous phase (Gong et al., 2018; Montuori et al., 2016). The LMW PAHs (2-3rings) have an evident acute but relatively low toxicity, while HMW PAHs (4–6 rings) have chronic toxicity (Kennicutt et al., 1994; Witt, 1995). This means that both water and sediments' samples have high toxicity due to the high percentage of the HMW PAHs.

3.5. Principal components analysis (PCA) in water and sediment

PCA has proven to be the multivariate analytical approach for sources identification of PAHs in environmental source apportionment studies, transforming the complex original data into a number of new factors or variables, each reflecting a group of correlated variables in the dataset (Anh et al., 2020). The sum of the principal components, also known as summary indices (PC-1, PC-2... PC-n), from a particular PCA is always 100 %, and the most important components (PC1, PC2, etc.) are retrieved to explain the variances that occur in the original dataset.

The results of PC on water samples revealed three factors that explained 67.03 % of the variation in the data; the largest part of the

overall variance was allocated to PC1, PC2, and PC3, as seen in Fig. 6 A, with variances of 41.59 %, 13.91 % and 11.53 %, respectively. Fig. S4 A exhibited the 3D presentation of the PCA analysis for water samples. Principal component 1 (PC1), which represents LMW PAHs (Nap, Acy, Ace, and FI) and HMW PAHs (BaA, Chr, BbF, BaP, BghiP, IND) explained 41.59 % of the overall variance. The PAH Nap is the major constituent of diesel fuels and gasoline, which may be produced by incomplete combustion (Soltani et al., 2015). IND may be a byproduct of pyrolysis or incomplete fuel combustion (Jiang et al., 2009). The BghiP is indicative of automobile emissions (Liu et al., 2009). The Chr indicates coal combustion and other PAHs, such as Flu are mostly derived from the enormous volume of vehicle emissions (Tavakoly Sany et al., 2014). The principal component- 2 (PC2) and principal component- 3 (PC3) represent the PAHs groups of Flu, Pyr, BaP, and DBA and Ant, Flu, Pyr, Chr, and BbF, respectively. Table S3 show the eigenvectors and percentage of variance for the PCA analysis of water samples. There are negative loadings such as Nap, Chr, BbF, BkF, etc. for PC-2 and Acy, Fl, and BaA for PC-3. This suggests a negative relationship or correlation between these PAHs and other PAHs where they originated. The BaA and BbF may originate mostly from vehicle emissions and the burning of fossil fuels (Liu et al., 2009). Illegal waste (liquid and solid) dumping in the water system and direct wastewater discharge along the Euphrates system could also contribute to higher PAHs concentrations. The atmospheric deposition of dust containing PAHs into the river system could be another reason for elevated PAHs levels. Burning fossil fuels, particularly in metropolitan areas, due to using private power generators could increase the concentration of these compounds in the surrounding environments.

The PCA biplot and 3D (Fig. S4 B) representation of PCA analysis for the sediment samples is shown in Fig. 6 B, which depicts the PAHs load at PC1 and PC2 and PC3. In sediment samples, PC1 accounted for 26.60 % of the variance, and its representative PAHs were Nap, Acy, Ace, FI, BaA, Chr, BbF, BaP, BghiP, and IND. PC2 accounted for 18.55 % of the variance, with Flu, Pyr, BaP, and DBA being its representative PAHs. The PC3 was responsible for 15.83 % of the variance in PAHs, including Ant, Flu, Pyr, Chr, and BbF. PC1 and PC3 exhibited a greater loading of both LMW and HMW PAHs, whereas PC2 had a greater loading of HMW PAHs. Table S4 shows the extracted eigenvectors values for sediment samples. Similar to the water samples, there is a number of negative correlations detected between the assigned PAHs for each component. According to PCA and diagnostic ratio, PAHs in the Euphrates River come predominantly from coal and fuel combustion, petrogenic, and pyrolysis sources.



Fig. 6. Biplots of the PCA analysis for (A) water and (B) sediment samples.

3.6. Source identification and Pearson's correlation coefficient of PAHs

To manage the emission and release of PAHs with greater precision, it is necessary to identify their sources of contamination to the full extent feasible. In general, there are four main sources of PAHs: geogenic, petrogenic, pyrolytic, and biogenic (Traven, 2013). Several PAHs diagnostic ratios have broadly been utilized to determine the likely source categories of PAHs in ecosystems (Kapsimalis et al., 2014). HMW PAHs ratios such as BaA/(BaA + Chr) and Flu/(Flu + Pyr) are usually used because they are more stable than LMW ones. Thus, in order to conjecture the potential origins of PAHs, the ratios of Ant/(Ant + Phe) and BaA/(BaA + Chr) against Flu/(Flu + Pyr) were graphed in Fig. 7. According to the results summarized by Yunker and his colleagues, a BaA/(BaA + Chr) ratio <0.2 indicates that oil emissions are the primary source of PAHs pollution. A ratio >0.35 indicates that combustion is the dominant source. A ratio between those two figures indicates a mixture of oil and combustion pollution (Yunker et al., 2002). The Ant/(Ant + Phe) ratio of <0.1 indicates contamination of petroleum origin, while Ant/(Ant + Phe) > 0.1 suggests pyrogenic sources (Lee et al., 2021). On the other hand, the Flu/(Flu + Pyr) ratio of <0.4 indicates contamination of petroleum origin or oil spills. A ratio of 0.4 < Flu/(Flu + Pyr) < 0.5 suggests petroleum combustion sources and a Flu/(Flu + Pyr) ratio of >0.5 indicates biomass combustion sources (Ontiveros-Cuadras et al., 2019). The ratio of LMW/HMW and the proportion of isomers with similar physicochemical properties could qualitatively represent the characteristics of their contamination sources. An LMW/HMW ratio of >1.0 implies petroleum sources, whereas a ratio <1.0 indicates combustion sources (Soclo et al., 2000). BaP/BghiP ratio can also be used to further confirm the estimation of PAHs sources. A BaP/BghiP ratio of <0.6 suggests that PAHs originated from non-traffic emission, whereas a ratio of >0.6 indicates that the source is traffic emission (Gbeddy et al., 2021). In addition, Pearson's correlation coefficient was also utilized to check for possible correlations between the 16 PAHs measured in this study as discussed in the following section.

3.6.1. Source identification and Pearson's correlation coefficient of PAHs in water

In water samples, except for S5, S6, S10 and S13, PAHs sources were mainly petroleum combustion (0.4 < Flu/(Flu + Pyr) < 0.5). S5 exhibited petroleum origin, and S6, S10 and S13 showed biomass combustion sources. By applying the ratio BaA/(BaA + Chr) for the water samples, it can conclude that S1-S3 values were between 0.2 and 0.35, which indicated a mixture of oil and combustion pollution. Nevertheless, other sites (S4-S13) indicated combustion with a ratio of >0.35. Assessing the

water samples along the entire river, an LMW/HMW ratio value of less than one was found for water samples indicating that combustion is the main source of PAHs compounds. Based on BaP/BghiP ratio criteria, PAHs in water samples S4-S10, S12 and S13 are likely to be originated from traffic emissions, while for other sites S1-S3 and S11, they were of non-traffic emissions origin.

From the matrix of Pearson's correlation coefficient, it is evident that there is a positive association between the 2–3 rings PAH ($R > 0.57$, $p < 0.05$) in water samples. For instance, Nap has a strong positive connection with Acy and FI. In addition, the coefficients between 2 and 3 rings PAHs and 5–6 rings PAHs were shown to be quite positive, with $r > 0.70$. This clearly can be seen via a positive correlation between Nap and Ace and other 5–6 rings PAHs such as BbF, and BghiP. In addition, Acy as a (2–3 rings PAH) was also positively correlated ($R = 0.82$) with 5–6 ring PAHs (BghiP and IND). In addition, it was discovered that PAHs compounds with 4-ring structures, such as Chr has very strong interactions with 5–6 rings PAHs such as BbF, BghiP and IND, with R-value of 0.81, 0.55 and 0.57, respectively. Between the 5–6 rings PAHs, IND has a strong correlation with BghiP, with an R-value of 0.83.

3.6.2. Source identification and Pearson's correlation coefficient of PAHs in sediment

In sediment samples, PAHs in S1, S4, S5, S7, S12 and S13 are suggested to be originated mainly from petroleum combustion (0.4 < Flu/(Flu + Pyr) < 0.5), while S8 and S11 exhibited petroleum origin, and other sites showed biomass combustion sources. Moreover, the BaA/(BaA + Chr) ratio is >0.35, which indicates combustion as a dominant source. Assessing the sediment samples along the entire river, an LMW/HMW ratio value of <1 was found, indicating that combustion is the main source of PAHs compounds. Regarding BaP/BghiP ratio, S1, S4-S7, and S8-S13 had PAHs originating from traffic emissions. For other sediment sites (S2, S3 and S8), PAHs were derived from non-traffic emissions.

Regarding Person correlation coefficient in sediment samples, Nap and FI, as well as Ace and Ant have a positive interaction with R values of 0.64 as well as 0.72, respectively. Other 2–3 rings PAHs, such as Phe and Ant have a link with BbF. Moreover, 4-ring PAHs such as Flu has a positive interaction with 5–6 rings PAHs such as DBA. IND was positively correlated with other 4–5 rings PAHs such as BbF and DBA. In general, the number of positive correlations between the PAHs groups is higher in water samples compared to sediment samples.

Based on the above-mentioned criteria, it can be noticed from Fig. 7 and Fig. 8 that PAHs generally in both water and sediment samples are derived from pyrogenic sources. Pyrogenic PAHs are combustion

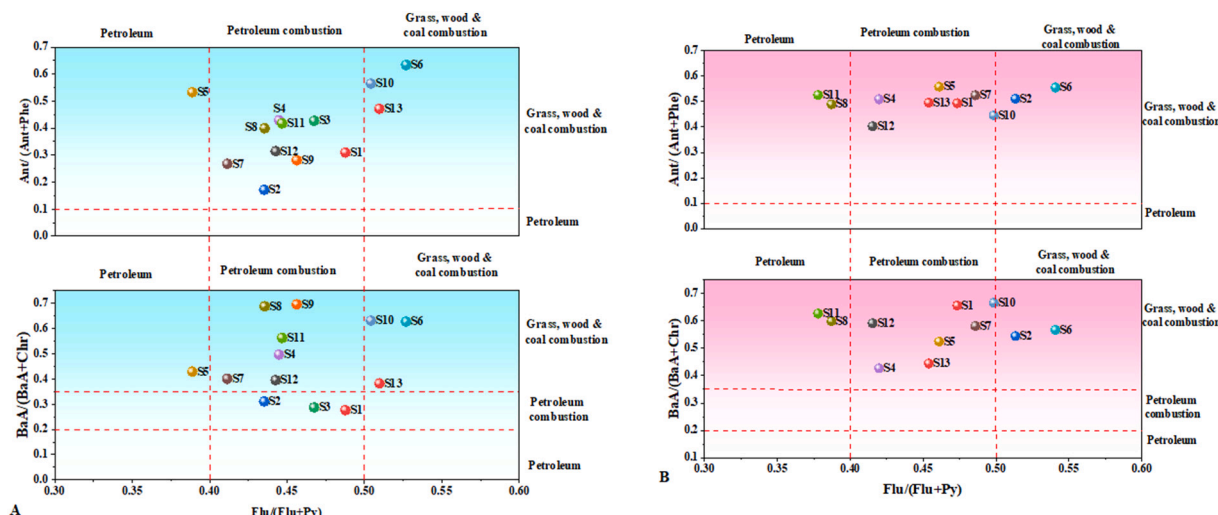


Fig. 7. Cross plots of PAHs source identification for (A) water and (B) sediment samples.

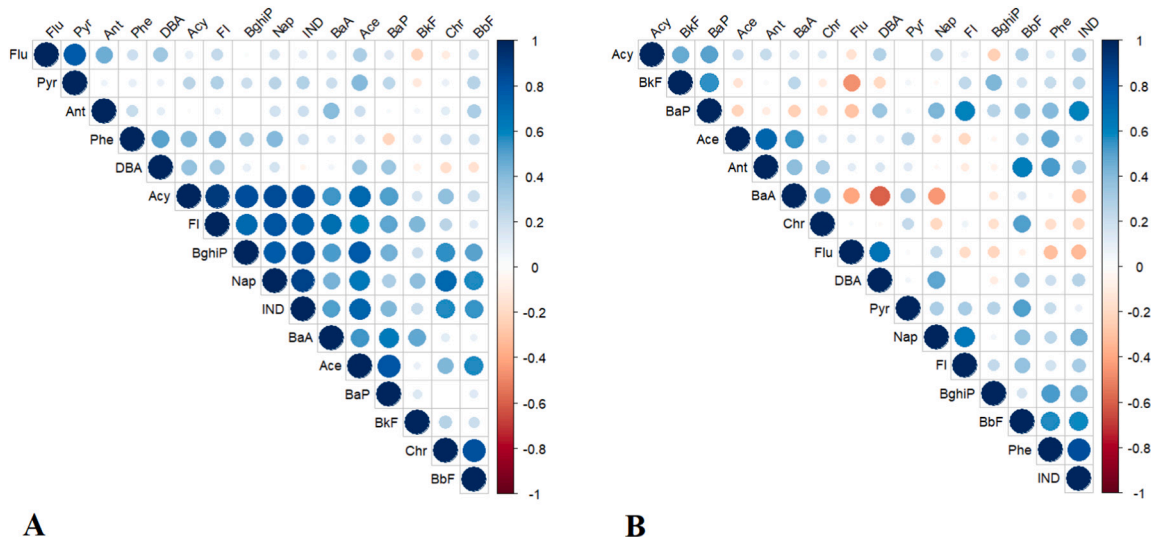


Fig. 8. Pearson correlation coefficients of the 16 measured PAHs for water (A) and sediment (B) samples.

byproducts that are mostly produced into the atmosphere by the combustion of fossil fuels (coal, petroleum, and wood) and biomass (forest, grassland, or agricultural) (Lima et al., 2005). Overall, the ratios revealed that pyrogenic sources dominated the 16 PAHs production in the Euphrates River system. This could be explained by a number of sources observable on the ground, including emissions from significant traffic load, gas and fuel combustion, home electricity generators, coal, and wood combustion.

3.7. Ecological risk assessment

The ecological risks of the PAHs posed to the Euphrates River system were evaluated using water and sediment qualities. The USEPA surface water quality standards have been adopted in this study as the Iraqi standards were more generic and only specify limits for hydrocarbons (10 µg) (EPA, 2018; IQS, 2009). Table S5 shows the PAHs measured concentrations in all locations benchmarked against their counterparts in the USEPA surface water quality standards. Based on this benchmarking, the total concentration of the PAHs measured in the collected samples was at was 8–18 times higher than the specified limit in the standard. This indicates a serious ecological risk to the aquatic life in the Euphrates River. However, the EPA safe standard limits for human health protection from some individual PAHs such as Ace, Ant, Flu, FI and Pyr were in the mg/L, which is higher than the highest detected concentration in the Euphrates River. This means that the river water might be safe for limited recreational activities and not for others.

The ecological risk evaluation for sediments samples followed the procedure described by (Ambade et al., 2021). The levels of PAHs in sediments were compared to sediment quality guidelines (SQGs). By comparing the concentration of individual PAHs with the Effect Range Low (ERL) and Effect Range Median (ERM) values, the ecological risk to aquatic species from exposure to sediment-bound PAHs was also assessed. The SQGs includes three categories of chemical concentrations that define the levels of adverse chemical effects on biology, which are minimal effects range with a rare biological effect (<ERL), possible effects range with occasionally biological effects (≥ERL and <ERM), and probable effects range with frequent biological effects (≥ERM) (Long et al., 1995). Table S6 exhibited the concentration range of 16 individual PAHs and toxicity guidelines. The concentrations of Acy, Ace, FI, Phe, Flu, BaA, and BghiP in sediments in all sites were above ERL and lower than ERM and belong to a possible-effects range based on comparing with SQGs. The Ant concentration in the sediment in all sites was lower than ERL, whereas DBA was higher than ERM. Other PAHs such as Pyr,

Chr, BbF, BkF, and BaP were varying between a rare biological effect in some locations and occasionally biological effects in other locations. The results indicate that there is a possible effect range with occasionally biological effects of most of the measured PAHs in all sediments samples.

3.8. Potential carcinogenic risk assessment and incremental lifetime cancer risk (ILCR) for sediment

To evaluate the carcinogenicity of PAHs compared to BaP, the toxic equivalency factor (TEF) method was used to compute the BaP equivalence (BaP_{eq}) of PAHs (Nisbet and LaGoy, 1992). Due to its high carcinogenic potential, BaP has been designated as a reference chemical in the TEF calculation and given a value of 1 in order to assess the carcinogenicity of each PAH compared to BaP. The reported TEF for Nap, Acy, Ace, FI, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BghiP, and IND were 0.001, 0.001, 0.001, 0.001, 0.001, 0.01, 0.001, 0.001, 0.1, 0.01, 0.1, 0.1, 1, 1, 0.01, and 0.1 respectively (Nisbet and LaGoy, 1992). Other PAHs chemical compounds have their own TEF values based on their carcinogenicity relative to BaP. In this work, the toxic equivalent quotient (TEQ) of each site was determined using the following equations:

$$\text{BaPeq}_i = (\text{PAH}_i \times \text{TEF}_i) \quad (1)$$

$$\text{TEQ} = \sum_i^n (\text{PAH}_i \times \text{TEF}_i) \quad (2)$$

Where PAH_i is the concentration of each PAH and TEF_i stands for toxic equivalency factor.

Fig. S5 shows the TEQ calculations' results for water samples. It was found that the TEQ ranged between a minimum of 73.4 ng/L (S3) to a maximum of 171.3 ng/L (S13). The TEQ results for sediments samples are presented in Fig. S6. The maximum and minimum values were present in S2 (838.9 ng/g dw) and S12 (1933 ng/g dw). The obtained TEQ values for both water and sediments samples were much higher than the reported values for rivers in other countries such as Australia, India, and Pakistan (Duodu et al., 2017; Kurwadkar et al., 2022; Aziz et al., 2014). These elevated levels are alarming and a clear signal of the need for urgent environmental authorities' intervention.

A risk assessment of human exposure to PAHs in the river sediments was conducted using the ILCR model of the USEPA, which considered three major routes of human exposure to contaminants (i.e., ingestion, dermal contact, and inhalation of vapor or sediment/dust). This was necessitated by the daily reliance of the locals on the aquatic resources of the area (USEPA, 2009). ILCR is used to estimate the human

carcinogenic risk presented by exposure to PAHs in the environment (Wang et al., 2018). The overall carcinogenic risk was calculated by summing the hazards associated with the three exposure pathways. Table S7 and eqs. (3–6) represent the parameters and model formulas selected for the evaluation of ILCR, respectively (USEPA, 2009; USEPA (U.S. Environmental Protection Agency), 1989; NYS DOH (New York States Department of Health), 2007)

$$\text{ILCR}_{\text{ingestion}} = \text{CS} \times \text{IR}_{\text{ingestion}} \times \text{EF} \times \text{ED} \times \left(\text{CSF}_{\text{ingestion}} \times \sqrt[3]{\frac{\text{BW}}{70}} \right) \times (\text{BW} \times \text{AT} \times 10^6)^{-1} \quad (3)$$

$$\text{ILCR}_{\text{inhalation}} = \text{CS} \times \text{IR}_{\text{inhalation}} \times \text{EF} \times \text{ED} \times \left(\text{CSF}_{\text{inhalation}} \times \sqrt[3]{\frac{\text{BW}}{70}} \right) \times (\text{BW} \times \text{AT} \times \text{PEF})^{-1} \quad (4)$$

$$\text{ILCR}_{\text{dermal contact}} = \text{CS} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED} \times \left(\text{CSF}_{\text{dermal contact}} \times \sqrt[3]{\frac{\text{BW}}{70}} \right) \times (\text{BW} \times \text{AT} \times 10^6)^{-1} \quad (5)$$

$$\text{Carcinogenic risk} = \text{ILCR}_{\text{ingestion}} + \text{ILCR}_{\text{dermal contact}} + \text{ILCR}_{\text{inhalation}} \quad (6)$$

Where CSF is the carcinogenic slope factor, which is measured in $(\text{mg kg}^{-1} \text{ day}^{-1})^{-1}$. The CSF concentrations of BaP, as reported by the USEPA are 25, 7.3, and $3.85 (\text{mg/ kg}^{-1} \text{ day}^{-1})^{-1}$ for the chosen routes in this study, namely dermal contact, ingestion, and inhalation (Chen et al., 2013). CS is the sum of PAH concentrations converted to toxic equivalents of BaP using the Toxic Equivalence Factor (TEF) (in ng/g dw). The estimation of ILCR is primarily based on the detection of PAHs as BaP equivalent concentrations using the TEF of each PAH relative to BaP. This is the reference chemical compound having a TEF of one. The total ILCR is the sum of the three pathways, namely dermal contact, oral intake, and inhalation. If ILCR (unitless) is $<1/10^6$, it is deemed to be considered negligible, however, if it is above $1/10^4$, there is significant concern (US EPA, 2011). The inhalation component of the ILCR was found to be insignificant ($<10^6$), and hence it was removed. The ILCR levels for adults and children obtained for the Euphrates River sediment samples (Table S8) are significantly higher than those reported for Brisbane River in Australia (Duodu et al., 2017). If these levels are confirmed through long-term monitoring, the population living at the river basin need to be made aware through and measures should be implemented to minimize human contact with the sediments.

4. Conclusion and recommendations

This study presented a thorough investigation of the temporal and spatial variation of the PAHs compounds in the Euphrates River in Iraq. This is the first where the entire river was sampled from both water and sediments. It was found that the contamination with PAHs increased along the river. IND was the most prominent PAHs compound in water and sediment samples across all 13 sampling locations. Some of the measured PAHs concentrations were much higher than the reported levels in other countries in Asia and Oceania. PAHs source identification suggests that the PAHs pollution originates mainly from petroleum product consumption, which is expected given the increasing use of private cars and home electricity generators. The measured PAHs in water and sediment samples were predominantly large molecules with 5–6 rings in their structure. The elevated levels of PAHs detected in the Euphrates River system, especially the carcinogenic compounds seem to have potential ecological and health risks. This is an alarming issue that needs urgent attention from the environmental authorities of the countries sharing this water source. Strict environmental protection is urgently needed to control the pollution of the river. Longer term and

more extensive monitoring should be conducted. The information about such programs can provide directions for further research. Strong correlations were detected between some LMW and HMW PAHs, especially in water samples. Studying such relationships in the future might provide useful and deeper insights into the dynamics of these compounds.

Code availability

Codes are Available on request.

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CRedit authorship contribution statement

Ruqayah Ali Grmasha: Validation, Visualization, Conceptualization, Methodology, Data curation, Formal analysis, Funding acquisition, Investigation, Resources, Software, Writing - original draft, Writing - review & editing. **Marwan H. Abdulameer:** Investigation, Methodology, Validation, Conceptualization. **Osamah J. Al-sareji:** Validation, Data curation, Formal analysis, Writing - review & editing. **Zaid Al-Gazali:** Investigation, Methodology. **Raed A. Al-Juboori:** Validation, Methodology, Writing - review & editing. **Mónika Meiczinger:** Validation, Writing - review & editing. **Khalid S. Hashim:** Validation, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

This submission does not include any associated research data sets. The following explanation is provided: No data was used for the research described in the article.

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Appendix A. Supplementary data

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