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Ecological and human health risk assessment of polycyclic aromatic hydrocarbons (PAH) in Tigris river near the oil refineries in Iraq

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ABSTRACT

Recent Iraqi battles against ISIS in 2014 and 2015 resulted in the destruction or severe damage to several refineries' infrastructure. This, along with other factors, has led to the release and accumulation of a wide range of hazardous chemicals into the environment, for instance, polycyclic aromatic hydrocarbons (PAH). Thus, for the first time, a comprehensive 16 PAHs measurements campaign over the course of six months near the oil refineries along the Tigris River and its estuaries was investigated. The 16 PAHs concentrations in surface water and the sediments for the following oil refineries: Baiji, Kirkuk, Al-Siniyah, Qayyarah, Al-Kasak, Daura, South Refineries Company, and Maysan were examined. The overall findings indicated that the 16 PAHs concentrations ranged from 567.8 to 3750.7 ng/L for water and 5619.2–12795.0 ng/g for sediment. Water samples in South Refineries Company recorded the highest PAH concentrations while Baiji oil refinery registered the highest PAH concentrations in the sediment samples. The percentages of high molecular weight PAH (5–6 rings) in water and sediment samples were the highest, ranging from 49.41% to 81.67% and from 39.06% to 89.39% of total PAH for water and sediment, respectively. The majority of 16 PAHs measured in water and sediment samples of the Tigris River were derived from pyrogenic sources. Based on sediment quality guidelines (SQGs), most sites showed a possible effect range with occasional biological effects of most of the PAH concentrations in all sediments' samples. The calculated incremental lifetime cancer risk (ILCR) value was high risk with adverse health effects, including cancer.

1. Introduction

Water is one of the most important and precious resources on the planet. It is necessary for residential, agricultural, and industrial facilities in addition to being essential to human life. Owing to the rapid industrial growth and population expansion, water consumption has grown dramatically over the last several decades, resulting in the depletion of water resources. Water-intensive industries, such as petroleum refineries, paper manufacturing, textile factories, and leather tanneries, impose a substantial demand on natural water supplies (Sonwani et al., 2021). Among these industries, it has been noted that petroleum refineries are the most polluting industry since they emit a broad variety of harmful and persistent pollutants. For instance, aromatic hydrocarbons, hydrogen sulphides, and heavy metals are some of these pollutants. Humans, animals, and aquatic plants are negatively impacted by these contaminants if discharged untreated or insufficiently treated (Jafarinejad and Jiang, 2019). In a petroleum refinery, crude petroleum oil is refined to produce various useful products such as

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gasoline, petroleum naphtha, diesel, lubricating oil, kerosene, etc., using a variety of unit operations and processes, including crude desalting, atmospheric and vacuum distillation, hydrotreating, etc. (Varjani et al., 2017). These unit operations and processes demand a great deal of water (or steam), resulting in the production of a million gallons of petroleum refinery effluent (Jain et al., 2020). The quantity of wastewater generated from these operations exceeds the entire amount of crude oil processed by 0.4–1.6 times (Varjani et al., 2020). Under different upstream and downstream unit operations, 1.0 L of crude oil requires 0.47–7.2 L of water (Varjani et al., 2020). In 2050, global crude oil demand is projected to reach roughly 121.5 × 10^6 BPD (U.S. EPA, 2005). Therefore, 7800–29000 × 10^6 L/d of petroleum refinery effluent will be generated. About 80–90% of the water utilized in petroleum refineries is eventually discharged as effluent (Jafarinejad and Jiang, 2019).

Organs, including the liver, kidneys, respiratory tract, lungs, and skin of animals and humans have been documented to be negatively impacted by the pollutants contained in petro refinery effluent. Exposure to oil industry pollutants has been found to increase the risk of different cancer types such as bladder, breast, colon, and prostate (Williams et al., 2020). The stress oil contamination imposes on resources and its direct impact on some industries, such as fishing, can affect the mental health of people (Eklund et al., 2019). Polycyclic aromatic hydrocarbons (PAH), which are prominent pollutants of the oil industry, impose serious threats to human health and the environmental system. They have a significant effect on the neurological and respiratory systems (Neri et al., 2016). PAH such as phenanthrene, naphthalene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, and benzo (a) pyrene can cause cancer of the larynx and throat (Abbas et al., 2013). PAH diminishes the soil's oxygen dissolvability, and it also lowers soil permeability. In addition, Polyaromatic hydrocarbon-rich wastewater has a detrimental effect on plant growth (Sima et al., 2019).

There is a limited number of studies that addressed the growing pollution problem of the oil industry in Iraq; most of them focused on soil contamination. For instance, a recent study by AL-Saadi and co-workers has stated several issues regarding the Iraqi oil sector. Among them, the upstream and downstream production infrastructure of the Iraqi oil industries have been repeatedly damaged (especially pipelines) by wars and international sanctions, which have affected both refineries and wells. They have pinpointed poor management of oil wastes, which causes environmental contamination (AL-Saadi et al., 2022). By analyzing 25 soil samples, a study by Nematollahi and co-workers revealed the concentration of PAH in the area around the Erbil and Kirkuk refineries ranged from 212.8 to 12790.4 ppb (Nematollahi et al., 2022). Another investigation has measured the levels of 13 PAHs in 24 soil samples collected from the Ahdab oil field in Wasit province, Iraq. The total of 13 PAHs concentrations in this study ranged between 19 mg/kg and 855 mg/kg (Alawi and Azeez, 2016). There are other local reports on the same issue, but because they lack scientific rigor, they have not been reported in the background of this study. In addition to the above studies, a recent report by BBC titled 'cancer is rife' concluded that there are significant PAH compounds in the blood samples of Iraqis living nearby the oil industry facilities (BBC, 2022).

The main surface water resources in Iraq are the Euphrates and Tigris rivers. These two water bodies are the most affected by oil contamination. This study is dedicated to examining the 16 PAHs levels in surface water and sediments along the Tigris River and its estuaries that are in proximity to oil industry facilities. Locations near the following oil refineries: Baiji, Kirkuk, Al-Siniyah, Qayyarah, Al-Kasak, Daura, South Refineries Company, and Maysan were investigated. The occurrence, sources, ecological and human health risks of these compounds are scrutinized in this work. To the authors' knowledge, this is the first study that conducted a lengthy sampling campaign for a large area with the aim of studying the contamination of oil-generated PAH of the surface water and sediment in the Tigris River. The study aimed to draw national and international attention to the deteriorating environmental situation of the water sources in Iraq caused by the oil industry. Sophisticated data analysis techniques and diagnostic ratios are implemented to understand the distribution of 16 PAHs in water and sediment samples.

2. Materials and methods

2.1. Chemicals and reagents

HPLC-grade solvents included ethyl acetate, methylene chloride, methanol, hexane, and acetone. All of them with a minimum purity of 99% were purchased from Fisher Chemical Co. (USA). Reference standards of 16 PAHs (QTM PAH-Mix, 2000 g/mL) as illustrated in Table S1 with its acronyms, and the chemical structures purchased from Supelco (Bellefonte, PA, USA). Silica gel (desiccant 2–5 mm), PAH recovery standards, sodium sulfate anhydrous as well as solid-phase extraction membranes (ENVI™-18 DSK SPE Disk, diam. 47 mm) were purchased from Sigma-Aldrich. Sodium sulfate anhydrous as well as silica gel heated for 4 h at 500 °C in a furnace oven to remove moisture or organics before being stored in a desiccator until further investigations. A Milli-Q water (18.2 MΩ cm resistivity at 25 °C and a total organic carbon below 5 ppb) was used for the experiments. The glassware was sanitized using ultrasonic cleaners (Heidolph™, Fisher Scientific) before being washed with n-hexane as well as acetone.

2.2. Sites description, collection, and analysis

2.2.1. Case study

Iraq's oil refineries are the fifth-largest in the world in terms of proven crude oil reserves and the seventh-largest in terms of oil production volume when compared to the US, Russia, and China (AL-Saadi et al., 2022). As of February 2021, Iraq's total nameplate (design) refinery capacity was about 1.2 million barrels per day; however, the effective capacity is around 900,000 barrels per day. The gap between planned capacity and actual capacity at the northern refineries is mostly due to the turmoil caused by ISIS attacks in 2014 and 2015, during which facilities were destroyed or severely damaged. Since 2015, a part of the capacity has been restored, including a section of the Baiji refinery. The Iraqi refineries generate extra heavy fuel oil and insufficient gasoline and diesel to fulfill local demand. To overcome local product shortages, some refined oil products are imported. In 2021, the South Refineries Company expanded its Basra refinery by 70 thousand barrels per day. In this work, twelve locations near oil refineries along the Tigris River and its estuaries were selected in Iraq, namely Al-Kasak oil refinery (S1), Qayyarah, before the oil refinery (S2), Qayyarah, after the oil refinery (S3), Kirkuk oil refinery (S4), Al-Siniyah (S5), Baiji before the oil refinery (S6), Baiji after the oil refinery (S7), Daura before the oil refinery (S8), Daura after the oil refinery (S9), Maysan oil refinery (S10), South Refineries Company, before Shatt Al-Basra Electricity gas station (S11), and South Refineries Company, after Shatt Al-Basra Electricity gas station (S12). South Refineries Company sometime refers to just South Refineries. Monthly samples from July to December 2022 of surface water and sediment were taken. Fig. 1 illustrates the sampling sites' coordinates. The sample sites' coordinates are provided in the supplemental materials (Table S2).

The studied oil refineries capacities in 2021 are as follows (design, effective capacity, numbers in thousands): (310, 140), (56, 56), (30, 20), (20, 14), (10, 10), (210, 140), (210, 210), and (40, 40) for Baiji oil refinery, Kirkuk oil refinery, Al-Siniyah oil refinery, Qayyarah oil refinery, Al-Kasak oil refinery, Daura oil refinery, South Refineries Company and Maysan oil refinery respectively (U.S. Energy Information Administration, 2021). Taking into consideration the above oil refineries in Iraq and considering daily continuous waste disposal into a nearby water body with its poor waste treatment, this could result in a concerning increase in the accumulation of a wide variety of toxic pollutants in the environment.

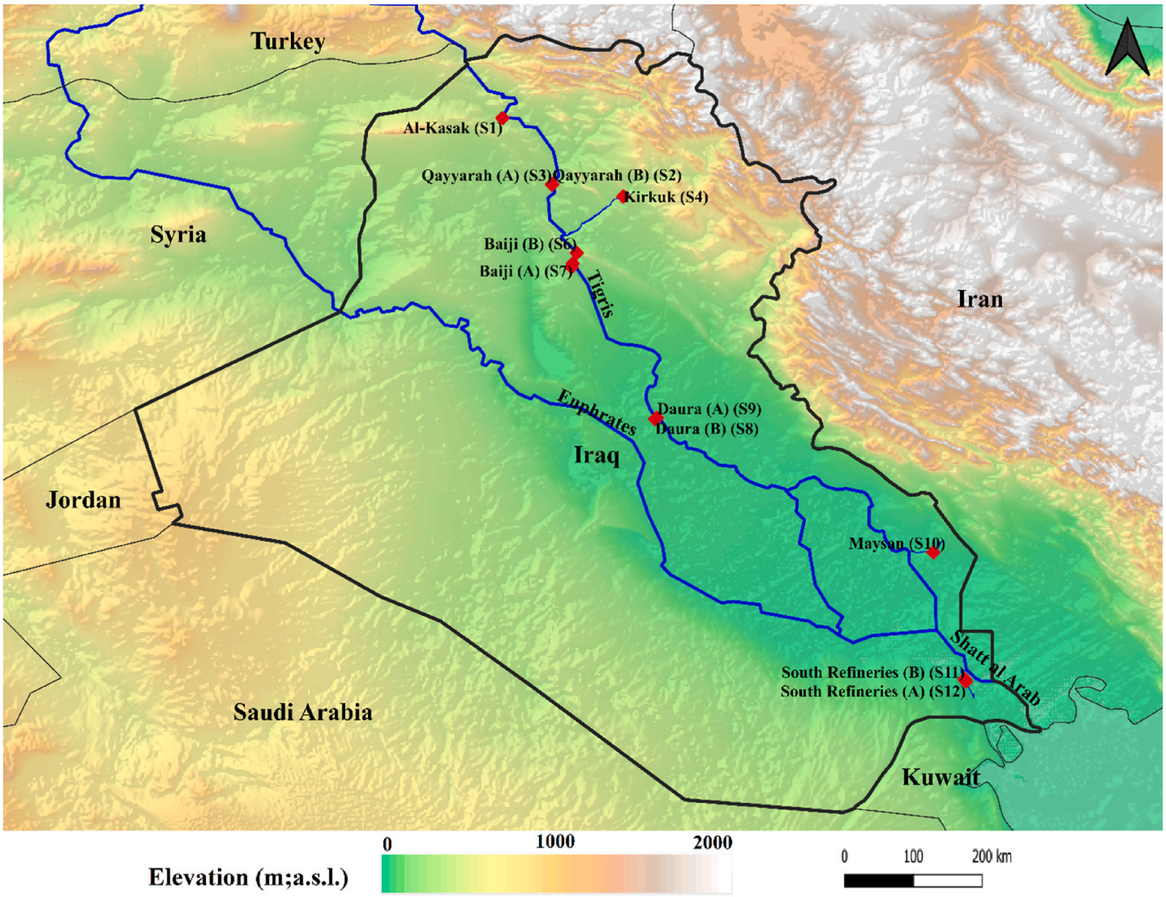

Fig. 1. Sampling site locations near the Iraqi oil refineries in the Tigris River and its estuaries.

2.2.2. *Collection and analysis*

The methodology used in this work followed the techniques described by (Dong et al., 2022; Grmasha et al., 2023; Lin et al., 2018). During the sampling campaign timeframe (from July to December 2022), each location was measured six times. Water samples were obtained between 20 and 40 cm below the surface via a stainless-steel container that had been previously cleaned. Samples were spiked with surrogates (naphthalene-d_8, anthracene-d_{10}, fluoranthene-d_{10} and perylene-d_{12}), the PAH recovery standard, sealed in five litter glass containers, transferred to the laboratory within 24 h, and refrigerated at a temperature of 4 °C until further measurements. Five litter of surface water was filtered via a 0.45 m glass fiber membrane and a methanol-activated solid-phase extraction (SPE) membrane in order to isolate PAH for analysis. In accordance with the procedures outlined by (Lin et al., 2018), the SPEs containing PAH were subsequently wrapped with aluminum foil and refrigerated before further measurements. Sediments were gathered and preserved in freezer-sealed bags. Three sediment samples (0–10 cm) were obtained via a grab sampler at the same site, then combined and kept in dark glass bottles. The samples were then immediately transferred to the laboratory for further investigations. The PAH were extracted from the SPEs using a technique that has been previously described (Lin et al., 2018; Ternon and Tolosa, 2015). SPE membrane was eluted with dichloromethane-ethyl acetate and ethyl acetate solutions twice. The extracts were mixed, dried over anhydrous sodium sulfate, concentrated using a rotary evaporator, and then redissolved in 1 mL of n-hexane.

Four grams of dry-frozen samples were properly weighed for the purpose of sediments extractions, sieved with 100 stainless steel mesh, then spiked with surrogates, put in an extract tube that contained 50 mL of a 1:1 mixture of acetone and hexane, and extracted using microwave digestion system. At a rate of 8 °C/min, the temperature increased from 25 to 120 °C and was maintained for 20 min. The samples were then subjected to a centrifuge for 20 min at 1000 rpm. After passing the supernatants through anhydrous sodium sulfate, a glass chromatography column was used to extract and purify them. After evaporating the samples to a volume of roughly 2 mL, 1 mL of n-hexane was added for analysis.

As detailed in our prior study (Grmasha et al., 2022), 16 PAHs were measured using gas chromatography-mass spectrometry (GC–MS) type Agilent 6890 N 5975C mass selective detector, USA. For GC–MS measurements at 1.5 mL/min using HP-5MS gas chromatography column (30 m 0.32 mm 0.25 μm), helium was employed as the carrier gas. The injector temperature was adjusted to 300 °C, and quantitative analysis was performed using selective ion scanning (SIM) mode. The temperature of the oven was set as follows: the beginning was 100 °C for 1 min, and then rose by 8 °C each minute to 300 °C, where it remained for 40 min.

2.3. *Quality control*

Glassware was heated to 100 °C before each measurement as well as cleaned with acetone, methanol, and dichloromethane to remove background contamination. The quantitative standards for 16 PAHs in the water sample were established using external standard techniques. For 16 PAHs monomers, the linearity correlation values ranged from 0.997 to 0.998. The 16 PAHs levels in sediment samples were carried out by using the dry weight method. The limits of detection (LOD) were carried out using analyte concentration and obtained using a 3-fold signal-to-noise ratio (Zhu et al., 2015). The LOD range for water was between 0.06 and 0.35 ng/L, while the LOD range for sediment was between 0.13 and 0.75 ng/g dry weight (dw).

In order to undertake recovery processes, the 16 PAHs standard solutions were spiked into water and sediment samples (Zhu et al., 2015; Wang et al., 2015). For each sample, a method blank (solvent), a spiked blank (standards added into solvent), and sample triplicates were performed. Method blank analysis demonstrated the absence of any detectable PAH contamination. The recovery ranges of water and sediment samples for 16 PAHs were 93.20%–100% and 85.30%–98.80%, respectively. The recovery ranges of the spiking standards were 94.50%–110.40% for water samples and 89.30%–96.60% for sediment samples. Concentrations of 16 PAHs were adjusted for recovery. To verify the accuracy of the analysis, blank and reference samples were measured. In addition, each sample was measured in triplicate, resulting in a relative standard deviation of less than 4%. The mean values were presented for the work. At a significance level of 0.05, the Kolmogorov-Smirnov normality test was used for all the data in this investigation.

3. Results and discussion

3.1. Surface water and sediment PAH range in each location

Fig. S1 depicts the changes in the 16 PAHs concentrations in the water samples within the course of six months (July–December 2022). The ∑16 PAHs in examined sites ranged between 678.2 and 718.5 ng/L for Al-Kasak (S1), 1080.2–1354.6 ng/L for Qayyarah (S2) (before the oil refinery), 3033.0–3263.9 ng/L for Qayyarah (S3) (after the oil refinery), 501.7–606.7 ng/L for Kirkuk (S4), 571.7–694.2 ng/L for Al-Siniyah (S5), 1739.0–2101.2 ng/L for Baiji (S6) (before), 3110.0–3290.0 ng/L for Baiji (S7) (after), 1141.9–1577.5 ng/L for Daura (before) (S8), 2690.2–2984.5 ng/L for Daura (after) (S9), 897.7–1040.5 ng/L for Maysan (S10), 1128.7–1502.3 ng/L for South refineries company (before) (S11) and 3614.6–3861.9 ng/L for South refineries company (after) (S12). Overall, within the field observations and as evident from the PAH measurement, it can be stated that there was high pollution in the surface water along the Tigris River and its estuaries with relatively heavily contaminated locations, especially after the oil refineries. The closer the refinery was to the water, the higher the pollution potential was, indicating improper waste management strategies.

The variation of PAH concentration in the sediment samples is shown in Fig. S2. The ∑16 PAH in examined sites ranged between 8224.8 and 9455.8 ng/g for Al-Kasak (S1), 5313.8–5942.0 ng/g for Qayyarah (S2) (before the oil refinery), 12037.2–13920.4 ng/g for Qayyarah (S3) (after the oil refinery), 6053.8–7241.2 ng/g for Kirkuk (S4), 7545.1–9575.8 ng/g for Al-Siniyah (S5), 6916.4–7466.6 ng/g for Baiji (S6) (before), 11321.2–13156.8 ng/g for Baiji (S7) (after), 5285.9–6260.8 ng/g for Daura (before) (S8), 11675.0–14089.9 for Daura (after) (S9), 7642.1–9718.8 ng/g for Maysan (S10), 5337.8–6025.5 ng/g for South refineries company (before) (S11) and 11318.2–13254.3 ng/g for South refineries company (after) (S12). Accordingly, the 16 PAHs concentrations in sediments followed the same trend as the 16 PAHs distribution in surface water, which also indicates that higher levels were observed after each oil refinery location.

3.2. Spatial and temporal variation of PAH concentrations in water and sediment

The overall findings of 16 PAHs found in water (A) and sediment (B) samples are shown in Fig. 2, which are recorded as mean PAH concentrations for each site. Sixteen PAHs were detected in all riverine sites, with concentrations ranging from 567.8 to 3750.7 ng/L for water and from 5619.2 to 12795.0 ng/g for sediment.

It can be seen in Fig. 2 (A) that all locations near the refinery have a high level of ∑16 PAHs in water samples, the concentrations doubled after the refineries locations as Qayyarah, Baiji, and South Refineries had the highest 16 PAHs after the refinery locations with ∑16 PAHs of 3203.0, 3192.5, and 3750.7 ng/L respectively. Fig. 2 (A) reveals that the most contaminated sites are S12, S3, S7, and S9. Phe, IND, BaP, and Bghip are the PAHs that were found in the highest concentrations at these sampling sites. Generally, because the sampling experiments were done from July to December, these six months are considered relatively warm periods in Iraq. Thus, HMWPAH were higher than LMWPAH in all sampling periods. This is connected to the fact that the variation in the patterns of PAH in surface waters throughout various sample periods is connected with the PAH molecular weight and degradation, which is more evident during warm seasons (Marquès et al., 2016). In contrast to HMWPAH which have a poor water solubility and dissolution rate, and are hence more resistant to decomposition, LMWPAH are more soluble and degradable during warm seasons.

The same observation was noted in the same location with sediments samples with ∑16 PAHs of 12,795, 12484.8, and 12449.1 ng/g for Qayyarah, Baiji, and South Refineries respectively. The variance of PAH in the sediments of the Tigris River indicates that the concentrations vary with sampling sites, indicating the anthropogenic activities along the Tigris River, as well as with seasons, given that the samples were gathered at various periods and places. However, no significant differences were identified in the patterns of PAH in sediments corresponding to various sampling periods, indicating that spatial variation is more crucial than temporal variation in determining the PAH inputs in sediments. These observations may indicate the contribution of a petroleum discharge to the Tigris River. IND, Bghip and Bap consistently recorded the highest levels among all measured PAH. It can be seen from Fig. 2 (B) that the most contaminated sites are S3, S7, S9 and S12. The most dominant PAH that occurred in high concentration in almost all the river sampling sites are Phe, IND, BaP, DBA and Bghip. As for sediment samples, S1, S3, S7, S9, and S12 are the most contaminated sites which could be explained by the possibility of nearby source pollution. IND, Bghip, Bap and Chr consistently recorded the highest levels among all measured PAH in sediment samples.

PAH contamination in water and sediments from numerous river systems throughout the globe has been explored. The level of PAH was reported by Sun and colleagues, who studied the distribution and the origin of 16 PAHs in the Henan beach of the Yellow River in central

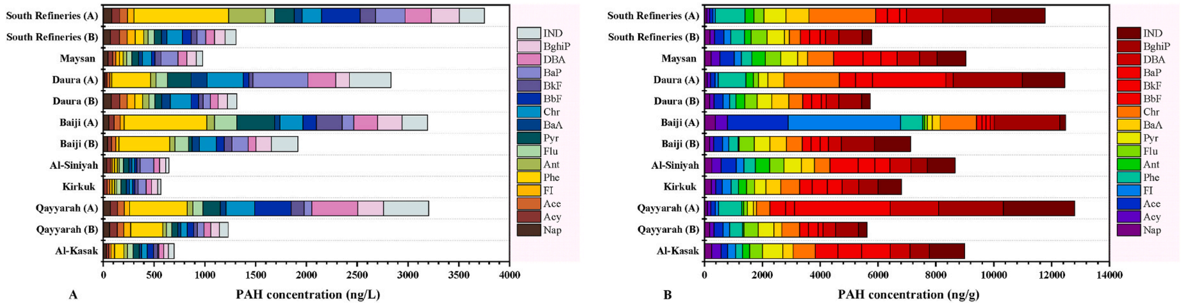

Fig. 2. Mean of the 16 PAHs concentration in water (A) and sediment (B) along the Tigris River. The letter (A) near the refinery name refers to the word after and the letter (B) represents the word before (before the refinery location).

China. They reported that PAH concentrations in water varied from 144.3 to 2361.0 ng/L, and in sediment from 16.4 to 1358.0 ng/g (Sun et al., 2009). Another investigation by Zheng and co-workers studied the pollution of surface water and sediment with PAHs in the estuary of the Daliao River and the surrounding region in China. In water, PAH concentrations varied from 71.1 to 4255.4 ng/L, and in sediment, from 374.8 to 11588.8 ng/g (Zheng et al., 2016). On the Cauca River in Columbia, the Prai River in Malaysia and Brisbane River, Australia, 16 PAHs concentrations of 15–3739 ng/g (dry weight), 1102–7938 ng/g (dry weight) and 148–3079 ng/g have been detected, respectively (Sarria-Villa et al., 2016; Keshavarzifard et al., 2014; Duodu et al., 2017). The higher PAH contents were mostly attributable to petrogenic and pyrogenic sources, as well as petroleum products and their combustion processes. In Egypt, 11 PAHs in sediment from the river Nile ranged from 4065 to 10,033 ng/g, which caused a high level of contamination (Omar and Mahmoud, 2017). The distributions, origins, and relationships of PAH and organic matter in sediments from the Duliujian and Beiyun rivers in northern China were investigated (Li et al., 2022). Sixteen PAHs were found in surface sediments ranging from 356 to 4652 ng/g dry weight, resulting in a moderate to high degree of contamination.

Chr, BaA, BaP, BbF, BkF, IND, as well as DBA, are the seven PAHs (7CPAHs) that the U.S. Environmental Protection Agency (USEPA) classifies as carcinogenic (Ekere et al., 2019). Fig. 3 shows the 7CPAHs along the twelve sites for water and sediment. About 33.5% (S2) to 64.5% (S9) of PAH in water were contributed by these hazardous chemicals. This is much greater than the range of 3.5%–28% of carcinogenic PAH observed in seven major Chinese rivers (Yu et al., 2015). BaP is the most cancer-causing substance. The concentration of BaP in the Tigris River ranges from 10.5 (S1) to 544.0 (S9) ng/L (mean = 149.8 ng/L), which is considered to be rather high. Baumard et al. (1998) categorized sediment PAH values as follows: low < moderate < high < very polluted when the PAH ranged from 0 to 100, 100–1000, 1001–5000, and more than 5000 ng/g, respectively. According to the categorization, the sediments of the Tigris are very polluted and need particular attention from the Iraqi government in order to reduce such significant concentrations.

3.3. Composition of 16 PAHs

3.3.1. PAH composition in water

Fig. 4 is a compositional diagram that displays the percentage of each group's composition in the water (A) and sediment (B) samples of the Tigris River. As for water samples, the HMWPAH (49.41% (S2) −81.67% (S9)) are more prevalent than the 4 ring PAH (18.33% (S9) - 50.59% (S2)). The high and low percentages of PAH in sampling locations could be explained by LMWPAH being more volatile and biodegradable as opposed to HMWPAH, which are more environmentally persistent (Adeniji et al., 2019). The prevalence of HMWPAH could be attributed to their non-bioavailability and low water solubility (Han et al., 2009). Han and colleagues concluded in their study that the high concentrations of HMWPAH compared to overall PAH concentration imply that they are a result of petroleum combustion (Han et al., 2009).

3.3.2. PAH composition in sediment

Fig. 4 (B) depicts the detected composition patterns of PAH with 2–6 rings in sediments. The majority of PAH in Tigris sediment samples were 5–6 rings PAH, accounting for between 39.06% (S7) and 89.39% (S3) of ΣPAHs. The 2–3 rings PAH comprised 10.61% (S3) to 27.94% (S11) of ΣPAHs, with the exception of S7, which included 60.94% of LMWPAH. The HMWPAH are more resistant to degradation and could thus be more efficiently transported and deposited in sediments. The acute toxicity of LMWPAH is observable but relatively low, whereas the chronic toxicity of HMWPAH is observable (Kennicutt et al., 1994). This indicates most samples are very hazardous due to the high concentration of HMWPAH. Overall, the PAH composition in water and sediment in the Tigris River was the same trend in our work in the Euphrates River, with an average of 42% and 50%, respectively, and the 5–6 rings PAH dominated in the water and sediment samples as well (Grmasha et al., 2023).

3.4. Principal components analysis (PCA) and source identification

3.4.1. PCA in water

Findings of PCA with respect to water samples indicated three variables, which described 84.89% of the variation. The majority of the variance was assigned to PCA1, PCA2, as well as PCA3, as shown in Fig. 5 (A), with variances of 49.21%, 24.94%, and 10.75%, respectively. PCA1 is laden with PAH from several sources, including oil combustion in gasoline and diesel engines and automobile emissions (Ramzi et al., 2017). In contrast, PCA2 and PCA3 are burdened with LMWPAH and molecules with 4–6 rings that show the existence of numerous contamination sources. PCA2 and PCA3 have negative loadings in terms of PAH compound. This shows that certain PAH have a negative link or association with other PAH. Direct discharge of wastewater and municipal waste disposal along the Tigris may also contribute to increasing PAH levels. Street dust deposition bounded by PAH compounds within the nearby areas could lead to elevated PAH levels as well in the Tigris River (Grmasha et al., 2022). The burning of fossil fuels,

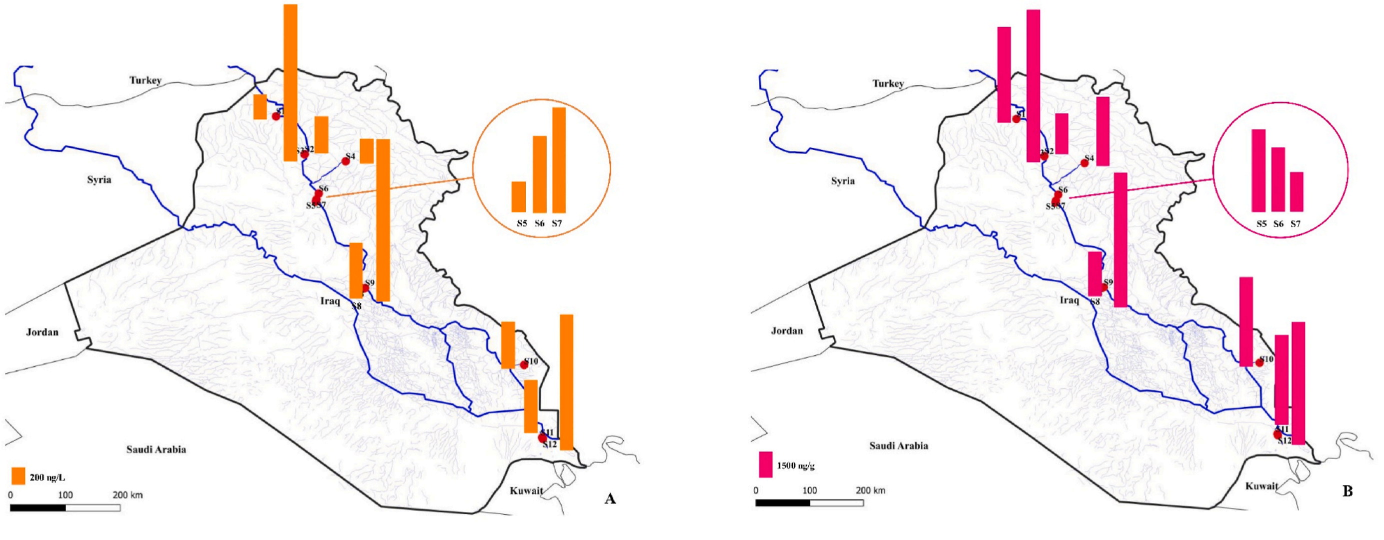

Fig. 3. 7CPAHs along the twelve sites for water (A) and sediment (B).

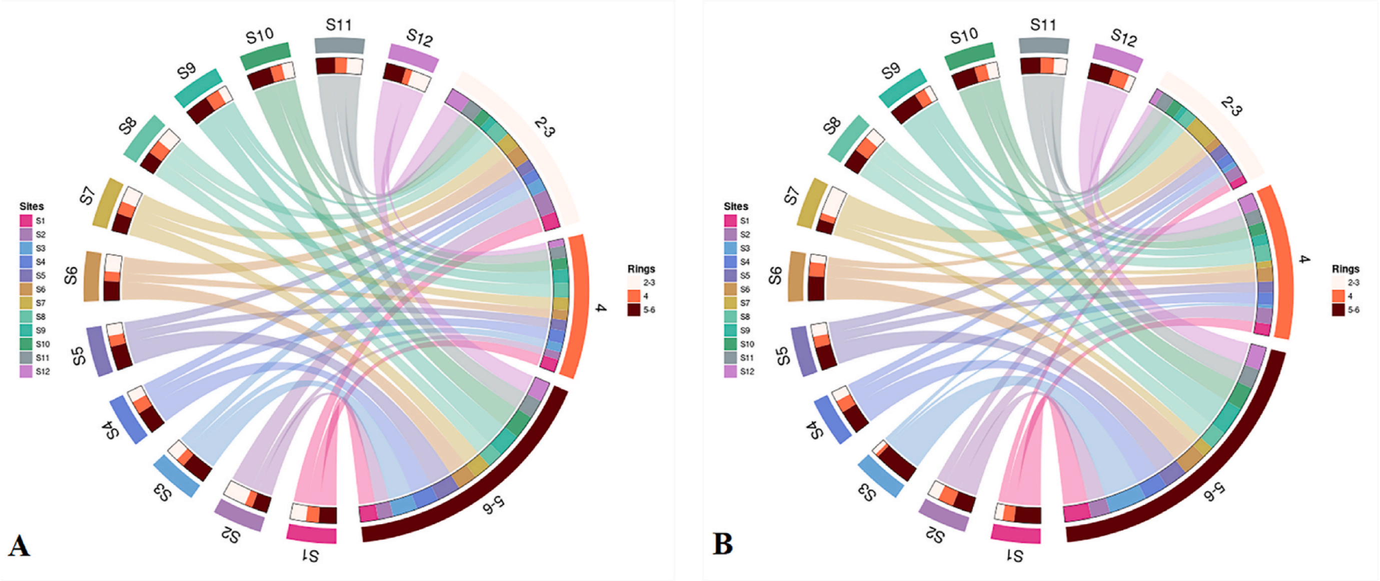

Fig. 4. PAH rings distribution for (A) water as well as (B) sediment.

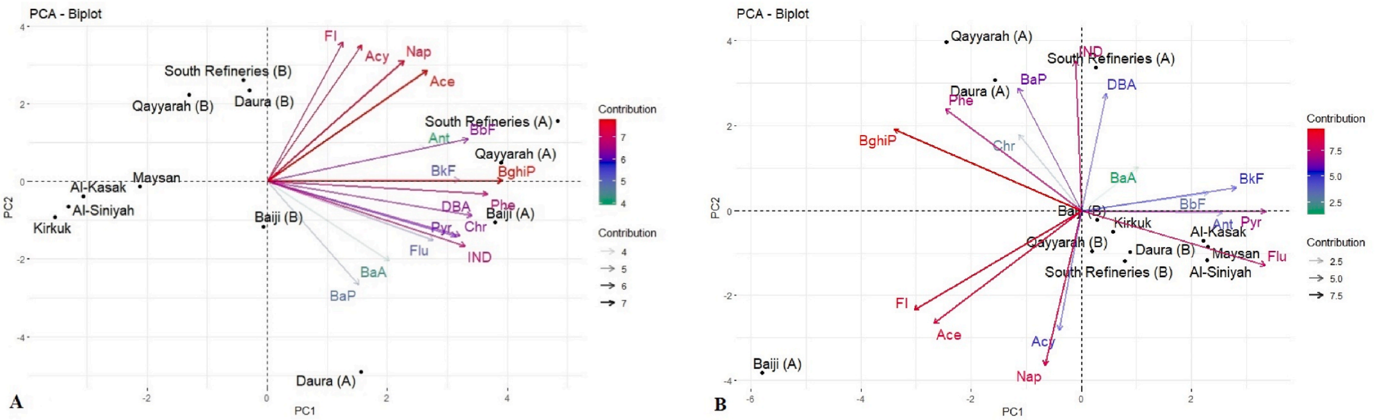

Fig. 5. Water (A) and sediment (B) results by PCA.

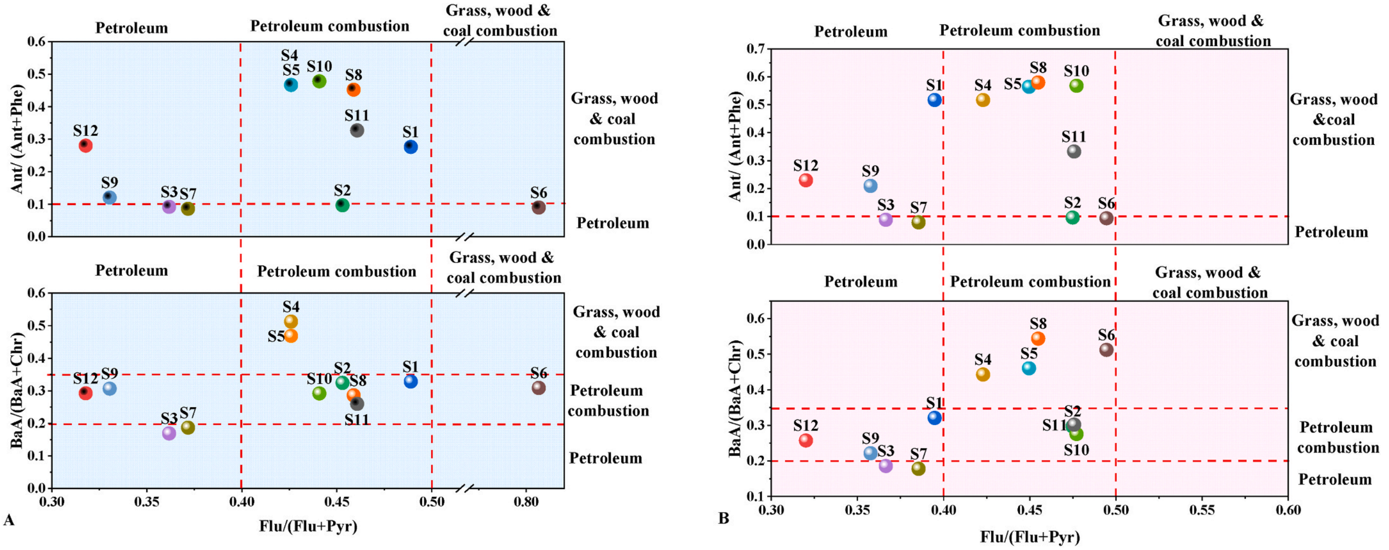

Fig. 6. Source identification of PAH in water (A) and sediment (B).

particularly by refineries, could boost the levels of toxic chemicals in the surrounding environment.

3.4.2. PCA in sediment

Fig. 5 (B) illustrates the PCA analysis of sediment samples, which illustrates the PAH load at PCA1 and PCA2, and PCA3 with a total of 75.16% of the variances. PCA1 accounted for 30.97% of the variation in sediment samples and is indicative of the majority of 4–6 ring PAH. PCA2 has a variance similar to that of PCA1, accounting for 29.89% of the variation, with 4–6 rings being its representative PAH. PCA3 accounted for 13.31% of the variation in PAH, including LMWPAH and PAH with 5–6 rings. Like water, a variety of negative associations between PAH ascribed to each component have been identified.

3.4.3. Source identification of PAH in water

Geologic, petrologic, pyrolytic, and biological processes are the primary sources of PAH (Traven, 2013). Text S1 discussed serval PAH diagnostic ratios applied in this work. Fig. 6 illustrates the ratios of Flu/(Flu + Pyr) against Ant/(Ant + Phe) and BaA/(BaA + Chr) for predicting the likely sources of PAH. In most sites, BaA/(BaA + Chr) ratio in water was between 0.2 and 0.35 which suggested a mixture of oil as well as combustion pollution. Similarly, both S3 and S7 exhibited a ratio of less than 0.2, indicating that oil-related activities were the predominant cause of PAH pollution. Site 4 and S5 exhibited BaA/(BaA + Chr) ratios greater than 0.35, indicating that combustion is the primary source of PAH contamination. Using the Flu/(Flu + Pyr) ratio, it is possible to deduce that S3, S7, S9, and S12 were less than 0.4, indicating oil contamination. Other locations (excluding S6) revealed sources of PAH from petroleum burning. LMW/HMW ratios of less than one was found for all river water sample locations except S2, indicating that combustion was the predominant source of PAH constituents. PAH in water S1, S3, and S7 are likely to be sourced from non-traffic origin depending on the BaP/BghiP ratio criteria, but PAH in other sites are likely to be released from traffic emissions.

3.4.4. Source identification of PAH in sediment

In samples from sites S4–S6 and S8, the BaA/(BaA + Chr) ratio was greater than 0.35, indicating that combustion is the primary source. Only sites S3 and S7 revealed oil as a source of PAH emissions, while other sites suggest a mixture of oil as well as combustion sources. PAH in S1, S3, S 7, 9 and S12 had ratios of Flu/(Flu + Pyr) less than 0.4, indicating pollution from petroleum or oil spills. Other places had PAH levels between 0.4 and 0.5, indicating petroleum combustion sources. In all areas along the Tigris River except S7, the LMW/HMW ratio was less than 1, suggesting that combustion was the primary origin of PAH. Applying BaP/BghiP ratio, S1, S3–S5, and S9–S10 included traffic pollution sources. PAH at other sediments areas were obtained from non-traffic-related sources.

PAH in water and sediment are often derived from pyrogenic sources, as seen in Fig. 6. Pyrogenic PAH are combustion byproducts primarily discharged into the environment by the burning of fossil fuels and biomass (Lima et al., 2005). In general, the ratios suggested which pyrogenic sources account for the majority of PAH found in the Tigris River. This might be linked to a number of physically observed sources nearby the Tigris River, such as oil refinery emissions, oil sector wastewater discharges, and oil combustion. In certain circumstances, such as the refineries in the south (S11 and S12), electrical generators for surrounding enterprises may be the primary PAH producers in the environment.

3.5. Ecological and health risks

The ecological risk assessment of sediment samples adhered to the methodology given by (Ambade et al., 2021). The 16 PAHs concentrations were evaluated according to sediment quality criteria (SQGs). Text S2 explained the categories of taken assessments. The concentration range and toxicity criteria for 16 individual PAH were included in Table S3. The levels of Flu and Acy in sediments at all locations were higher than the ERL but lower than the ERM, placing them within the range of possible effects range based on comparison with SQGs. At all locations, Ant concentrations were below the ERL, allowing for the assignment of minimal effects range with rare biological effects. PAH such as Ace, FI, DBA, and BghiP fell between the possible effects range with occasional biological effects and the probable effects range with frequent biological effects. Other PAH, including Nap, Phe, Pyr, BaA, Chr, BbF, and BkF, had either a rare biological impact in certain areas or an occasional biological effect in others. In the case of BaP, however, all SQG situations were presented. The findings reveal that the majority of PAH concentrations in all samples of sediments have possible effects range with occasional biological effects occurrence.

The ecological concerns posed by PAH to Tigris River water were evaluated in accordance with USEPA criteria for surface water quality, while Iraqi rules were more generic and merely prescribed hydrocarbon limits (10 μg) (IQS, 2009). According to USEPA regulations (standard limit ≤31 ng/L, as a total of Acy, BaA, BaP, BbF, BghiP, BkF, Chr, DBA, IND, and Phe), the PAH in the samples were much higher than the limit specified by the standard. This demonstrates that the aquatic life of the Tigris River faces a serious ecological danger.

The toxic equivalency factor (TEF) approach was employed to calculate the BaP equivalence (BaPeq) of 16 PAHs to assess their carcinogenicity relative to BaP (Nisbet and LaGoy, 1992). To determine the carcinogenicity of each chemical relative to BaP, the latter has been identified as a reference chemical in the TEF determination as well as assigned a value of one because of its high carcinogenic potential. The reported TEF for other PAH were illustrated in Table S1. Other PAH have their own TEF values depending on their carcinogenicity compared to BaP. Using the following equations, the toxic equivalent quotient (TEQ) of each location was calculated for this study.

$$\mathrm{BaPeq}_i = (PAH_i \times TEF_i) \tag{1}$$

$$\mathrm{TEQ} = \sum_{1}^{n} (PAH_i \times TEF_i) \tag{2}$$

Where PAHi is the chemical concentration and TEFi is the toxic equivalency factor.

The TEQ findings in water ranged from 79.6 ng/L for S1 and 890.4 ng/L for S9. The minimum TEQ value in the sediment sample was 414.0 ng/g for S7 and 5353.1 ng/g for S3. TEQ results were mostly higher than those observed in other areas, for instance, India, and Pakistan (Kurwadkar et al., 2022; Aziz et al., 2014). These worryingly high levels strongly indicate that immediate action by environmental authorities is necessary.

Using the USEPA's ILCR model, a risk assessment of human exposure to PAH in river sediments was performed. This was necessary because of the individuals' daily dependence on the region's aquatic resources (USEPA, 2009). ILCR is usually employed to quantify the human carcinogenic risk posed by environmental PAH exposure (Wang et al., 2018). The total carcinogenic risk was computed by adding the risks associated with the exposure routes. Table S4 and equations (3)–(5) describe the ILCR evaluation parameters and model formulations, respectively (USEPA, 2009, 1989). The ILCR values found in sediment samples from the Tigris River (Fig. S3) are much greater than those reported in Australia's Brisbane River (Duodu et al., 2017). Since these concentrations were detected by long-term monitoring, the individuals nearby the examined locations must be notified and precautions must be taken to limit human contact with the sediments.

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

$$\mathrm{ILCR}_{\mathrm{dermal\ adsorption}} = \mathrm{CS} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED} \times \left(\mathrm{CSF}_{\mathrm{dermal\ contact}} \times \sqrt[3]{\frac{\mathrm{BW}}{70}} \right) \times \left(\mathrm{BW} \times \mathrm{AT} \times 10^{6} \right)^{-1} \tag{4}$$

$$\text{Carcinogenic risk} = \mathrm{ILCR}_{\mathrm{ingestion}} + \mathrm{ILCR}_{\mathrm{dermal\ adsorption}} \tag{5}$$

Where CSF is the carcinogenic slope factor (mg $\mathrm{kg}^{-1}\mathrm{day}^{-1})^{-1}$. The CSF values of BaP, as stated by the USEPA, are 7.3, and 3.85 (mg/kg-$\mathrm{day}^{-1})^{-1}$ for the ingestion and dermal adsorption respectively. CS is the total of PAH concentrations that have been converted to toxic equivalents of BaP using the Toxic Equivalence Factor (TEF) (in ng/g). Table S4 represents the other parameters for equations (3) and (4). Determination of the ILCR is primarily dependent on the PAH as BaP-equivalent concentrations using the TEF of each PAH relative to BaP. It is the chemical compound with a TEF value of one. The total ILCR is equal to the sum of three routes: oral ingestion, inhalation and dermal absorption. If ILCR (unitless) is less than $1/10^6$, it is considered negligible; if it is more than $1/10^4$, there is cause for significant concerns (US EPA, 2011). The inhalation of PAH mostly comes from air breathing, whereas the inhalation of aquatic contamination should probably occur during an incident involving water choking (Bateni et al., 2022). Due to a low likelihood of accidental water choking, inhaling PAH in sediments in this investigation was omitted from health risk assessments. Thus, the only PAH exposure routes considered in this investigation are dermal contact and ingestion (Ihunwo et al., 2021). This was also considered in other works when ILCR was computed (Miao et al., 2023; Yu et al., 2015). Text S3 explained the non-carcinogenic risk and ILCR equations and parameters for water. The HI values (as non-carcinogenic) of PAH in the Tigris River water samples ingested intentionally suggest a low potential non-carcinogenic risk. Furthermore, the chronic exposure scenarios for unintentional water ingestion were all higher than the intermediate exposure. The determined ILCR values for water depicted in Figure S3 (A) indicated that all examined sites posed a high risk of carcinogenicity.

4. Sediment remediation and its proposed technologies

A typical scheme for remediating a polluted site, such as sediment in an aquatic ecosystem, consists of three stages: (1) site investigation and risk assessment, (2) selection of the most suitable remediation method, and (3) remediation and monitoring of the contaminated site (Maletić et al., 2019). The purpose of stage 1 is to determine whether or not the site has been PAH polluted, which involves location characterization and risk assessment, as well as determining whether the content of PAH exceeds the concentration specified in the regional or national standards. Then after this, the site is declared contaminated, and a management program should be implemented. The management program begins with a focus on source control to terminate PAH discharge. After determining the level of pollution, a detailed examination of feasible remedial options and the development of remediation strategies are implemented for the purpose of stage 2. In this stage, there are two techniques: in-situ and ex-situ remediations. In-situ is the process of treating pollutants at their source without relocating sediment. Ex-situ is performed away from the contaminated site. No matter which method is selected, the effectiveness of the chosen remedial option is predicted by laboratory and/or on-site feasibility and treatability studies. For the feasibility or treatability assessment of soil remediation, the amount of PAH that are desorbable from the soil matrix, bioluminescence-based biosensor assay, microbial survival test, microbial enumeration of PAH degraders, degradation rate, dehydrogenase activity, ecological impact and toxicity assessment, soil respirometric tests and tracking of inoculated organisms may be utilized (Diplock et al., 2009). The laboratory test outcomes are utilized in order to determine the most effective remedial action for a particular location. The final stage involves the implementation of approved technologies, long-term monitoring, and an evaluation of ecological and health risks (Duan et al., 2015). These technologies include the following, but are not limited to:

- Natural recovery: It utilizes natural physical, biological, and/or chemical procedures to limit, eliminate, or destroy the toxicity or bioavailability of sediment pollutants (EPA, 2005).
- Capping: This could happen from a layer of clean material, like sediment or sand (passive capping). It also could be introduced as sorbent substances derived from organic carbon-rich adsorbent (for instance, activated carbon, biochar and coke, organoclay, apatite, as well as zeolites and zerovalent iron), which are more efficient in minimizing pollutant transfer because they merge the effects of diffusive and sorptive barriers (active capping) (Silvani et al., 2017; Lofrano et al., 2017). Stabilization of polluted sediment, chemical isolation of polluted sediment, and/or physical isolation of polluted sediment are the three main functions of caping (EPA, 2005).
- Dredging: It involves the physical removal and transportation of the polluted sediment to the place of treatment and/or disposal (EPA, 2005). Generally, sediment treatment technologies are categorized as extraction or washing, thermal destruction or desorption, solidification/stabilization, as well as biological and chemical treatments.

5. Uncertainty and limitations

In PAH analysis, GC techniques are common because of their higher selectivity, sensitivity and resolution in comparison to liquid chromatography techniques. Separation and retention of PAH could be influenced via a variety of parameters, for instance, solvent effect, temperature programs, stationary phases, injection conditions, etc., which consequently impact the analysis precision and accuracy (Poster et al., 2006). Among these parameters, the stationary phase of GC is an essential component that has been studied. Although DB-5MS is one of the most commonly utilized capillary columns for PAH analysis, GC capillary columns with a higher phenyl content, such as a DB-17MS column with 50% phenyl-substituted methylpolysiloxane, demonstrated enhanced separation of high molecular weight PAH (Poster et al., 2006; Schubert et al., 2003). For example, it was stated that a DB-17MS column of 30 m was adequate for the separation of the majority of high molecular weight PAH, but a column of 60 m may be required for the separation of certain critical isomers (Schubert et al., 2003). In this investigation, PAH compounds were measured using an HP-5MS capillary column of 30 m, rather than HP-5MS column of 60 m due to the 60 m column's extended analysis duration. In addition, liquid chromatography with fluorescence detectors could be a replacement technique because of its own unique fluorescence properties (Sauvain and Vu Duc, 2004).

It should be noted that there were some limitations in isomeric ratios; for instance, in real multimedia environments, the paired isomers were (bio)degraded and transformed to various extents during the transport process, resulting in an overestimate of source allocation. Zhang et al. (2005) proposed an application of the multimedia fugacity model to calibrate isomeric ratio deviations. Their attempt was to quantify potential changes in PAH ratios from sources to bulk media, including PAH ratios on particles in air, sediment, suspended solids, and soil. This model requires comprehensive information on all source types and the chemical composition profile for each source, which is generally unavailable. Furthermore, the local combustion process affects both the isomer ratios and chemical composition profiles that are essential in receptor models. Ratios or profiles from various regions could be significantly different and unrepresentative of one another. Adding to that, due to the extremely high cost of multimedia sampling in a large area, like our study along the entire Tigris River, as well as some limitations on the pretreatment and analytical conditions, we used the specific ratios of paired isomeric species to diagnose the local emission sources of PAH in this study. Furthermore, PCA was utilized to aid in source identification.

6. Conclusion

The recent Iraqi battles against ISIS in 2014 and 2015 resulted in the destruction or severe damage to several refineries' infrastructure (especially the northern ones). Additionally, severe pollution come from these refineries, which suffer from fragile infrastructure, has led to an increase in the rate of cancer in Iraq as 40 million people are using this river in their daily activities. For these reasons, this study investigated the level of 16 PAHs near Iraqi oil refineries. Most of these refineries are located near the Tigris River and its estuaries, one of Iraq's most important sources of potable water and irrigation. The refineries examined were Baiji, Kirkuk, Al-Siniyah, Qayyarah, Al-Kasak, Daura, South Refineries Company, and the Maysan oil refinery. During six months, the 16 PAHs concentration in water varied from 567.8 to 3750.7 ng/L, whereas the concentration in sediment ranged from 5619.2 to 12795.0 ng/g, which registered a very high load of PAH compounds compared to other regions in the world. The PAH concentration in the downstream sites of the refineries Baiji, Qayyarah, Daura, and South Refineries Company was double the values of the upstream. The HMWPAH accounted for 49.41% - 81.67% and 39.06%–89.39% of the total 16 PAHs in Tigris water and sediment samples, respectively. The 16 PAHs detected in water and sediment samples from the Tigris River originated from pyrogenic sources. All sites indicated high incremental lifetime cancer risk (ILCR) values which exceeded the ILCR reported elsewhere. This study's finding is a call for immediate attention from the Iraqi government to act urgently by implementing plans to mitigate the risk of PAH contamination in the Tigris basin. It is also recommended to implement stringent pollutants discharge limits, especially for oil industry wastewater by upgrading the existing oil refineries waste treatment. Future studies are recommended on the followings:

- As oil refineries have a direct impact on both human health and the environment, it would be essential to conduct extensive, long-term studies for different multimedia near these refineries.
- Additional research is necessary to develop analytical methods and toxicological information for other nonpriority PAHs.
- Future research could assess the potential risk of PAHs in urban, suburban, and rural areas from economic and environmental perspectives.

Author contributions statement

Ruqayah Ali Grmasha: Formal analysis, Writing – original draft, Visualization, Writing – review & editing, Methodology, Investigation, Conceptualization, Resources, Funding acquisition, Software. Csilla Stenger-Kovács: Supervision, Writing – review & editing, Validation. Baydaa Abdul Hussein Bedewy: Methodology, Data curation. Osamah J. Al-sareji: Writing – review & editing, Methodology, Investigation. Raed A. Al-Juboori: Writing – review & editing, Methodology. Mónika Meiczinger: Writing – review & editing, Validation. Khalid S. Hashim: Writing- Reviewing and Editing, Methodology.

Statement from the authors

All claims, views, or opinions made in this manuscript are solely those of the authors and do not necessarily reflect those of their affiliated organizations, governments, oil refineries, other oil sectors, the publisher, editors, or reviewers.

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Code availability

Codes are publicly available.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

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