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PII: S0375-6742(24)00006-2

DOI: https://doi.org/10.1016/j.gexplo.2024.107390

Reference: GEXPLO 107390

To appear in: *Journal of Geochemical Exploration*

Received date: 3 July 2023

Revised date: 26 November 2023

Accepted date: 17 December 2023

Please cite this article as: H. Haghnazar, Y. Abbasi, R. Morovati, et al., Polycyclic aromatic hydrocarbons (PAHs) in the surficial sediments of the Abadan freshwater resources − Northwest of the Persian Gulf, *Journal of Geochemical Exploration* (2023), https://doi.org/10.1016/j.gexplo.2024.107390

Polycyclic aromatic hydrocarbons (PAHs) in the surficial sediments of the Abadan freshwater resources − Northwest of the Persian Gulf

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Abstract

This research focused on investigating the contamination levels, sources, and potential ecological and human health risks associated with 16 polycyclic aromatic hydrocarbons (PAHs) present in surficial sediments of the Abadan freshwater resources in the northwest of the Persian Gulf. The concentrations of ∑16PAHs varied between 67.8 to 57748 ng/g with an average of 8222 ng/g. Approximately 30% of the ∑16PAHs were attributed to seven carcinogenic PAHs. The predominant components of the PAHs found in the sediments were the 3- and 4-ring PAHs, which accounted for approximately 63% of the total PAHs present in the surficial sediments. The diagnostic ratios and principal component analysis (PCA) indicate that the PAHs detected in the sediments originated from various sources, including traffic emissions, coal, and biomass combustion, petroleum leakage, and wastewater. According to our ecological risk assessment, substantial harm to the biota was observed in the Arvand River. An assessment of cancer risk indicated that both adults and children in Abadan area are exposed to a considerable cancer risk due to the presence of PAHs. In conclusion, ongoing monitoring of PAH pollution and implement measures to protect freshwater ecosystems near the Persian Gulf are essential.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Surficial sediments; Arvand River; Petroleum; Ecological risk

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants that have become a major concern worldwide due to their persistence, toxic properties, and potential adverse impacts on both the environment and human health (Jafarabadi et al. 2019; Xu et al. 2021). PAHs are lipophilic contaminants containing two or more fused benzene rings, and they are formed through various natural and anthropogenic processes (Sun et al. 2017). PAHs are formed primarily through the incomplete combustion or pyrolysis of organic materials, and they are commonly associated with industrial activities, particularly those related to petroleum products, which contribute substantially to PAH pollution in the environment. (Yuan et al. 2014; Patel et al. 2020; Han et al. 2021;). PAHs are of particular concern in river ecosystems, as rivers act as conduits for transporting pollutants from land-based sources to coastal areas (Men et al. 2009; Tian et al. 2013). River sediments, characterized by their high affinity for PAHs and their role as long-term sinks, play a crucial role in the accumulation and storage of these contaminants (Santana et al. 2015; Ashayeri et al. 2018). Sediments can act as both temporary and long-term secondary sources of PAHs, as they can release the adsorbed PAHs back into the water column through processes such as sediment resuspension (Qiu et al. 2009; Liu et al. 2016; Lin et al. 2018; Hosseinzadeh et al. 2023). This dynamic behavior makes river sediments an important component in the cycling and fate of PAHs within aquatic systems.

PAHs can be classified into two categories based on their molecular weights: low molecular weight (LMW) and high molecular weight (HMW) PAHs (Abdollahi et al. 2013). LMW-PAHs typically consist of two to three aromatic rings, such as naphthalene and phenanthrene. These compounds are relatively small in size, have lower molecular weights, and are more volatile compared to HMW-PAHs. On the other hand, HMW-PAHs contain four or more aromatic rings, such as pyrene

and benzo[a]pyrene. The HMW-PAHs are larger in size compared to LMW-PAHs, have higher molecular weights, and are generally less volatile (Zeng et al. 2018). LMW-PAHs are more soluble in water and can readily enter the atmosphere, whereas HMW-PAHs tend to be more hydrophobic and have a greater tendency to adsorb onto particles or sediment (Niu et al. 2021). The differences in their physicochemical properties and behavior also contribute to variations in their toxicity and potential effects on human health and the environment. In aquatic ecosystems, PAHs can bioaccumulate in organisms, leading to adverse effects on the entire food chain (Pozo et al. 2011). Some PAHs have been shown to be mutagenic and genotoxic, increasing the risk of DNA damage and the development of various types of cancer, including lung, liver, bladder, and skin cancer (Ma et al. 2019; Huang et al. 2019; Ravanbakhsh et al. 2022). Certain PAH compounds have the potential to disrupt the endocrine system, leading to hormonal imbalances and reproductive disorders (Kakavandi et al. 2023; Lee and Choi, 2023). Additionally, PAH exposure during pregnancy may pose risks to the developing fetus, potentially causing developmental abnormalities and long-term health effects (Drwal et al. 2019; El-Sikaily et al. 2023). PAHs can also negatively impact the health of benthic organisms residing in sediment, as they can be absorbed through the skin and affect physiological processes (Pheiffer et al. 2018).

Abadan city, located near the northwest of the Persian Gulf, hosts one of the largest oil refineries in the Middle East. In addition, the region has several industrial factories, and is characterized by high vehicle traffic loads. They both contributes to substantial PAHS pollution sources in the region (Mohammad Asgari et al. 2023). The petroleum emission and leakage in this area contains a complex mixture of organic compounds, including highly toxic PAHs, which accumulate in the local sediments over time and are eventually transferred downstream to Persian Gulf via sediment transport. Therefore, understanding the levels, distribution patterns, and sources of PAH pollution

in the local river sediments is crucial for assessing the environmental risks associated with these compounds and developing effective mitigation strategies. To the best of our knowledge, this research presented an updated comprehensive study on the Abadan freshwater resources considering three rivers and covering all potential sources of PAHs.

Accordingly, the main research objectives are (1) quantify the concentrations of PAHs in surficial sediments of the freshwater resources within Abadan city; (2) analyze the spatial distribution and potential hotspots of PAHs contamination; (3) identify the major PAH compounds and their respective sources; and (4) evaluate the ecological and health risks associated with PAH pollution in the study area.

Our findings are of value to policymakers, environmental authorities, and local communities in mitigating the risks posed by PAH pollution, protecting the freshwater ecosystems, and ensuring the sustainable use of these vital resources near the Persian Gulf.

2. Materials and methods

2.1. Study area

Abadan, located in the southwestern region of Iran's Khuzestan province, is the largest industrial city in the area. Its coordinates are approximately 30° 20′ 40″ N and 48° 17′ 20″ E. As of 2016, it had a population of around 347,000. The climate of the study area can be described as semi-arid, with extremely high temperatures in the summer and mild temperatures in the winter. The annual precipitation is 157 mm, and the temperature ranges from -2.2°C to 52.3°C. Abadan is bordered by the three main rivers of Khuzestan province: the Arvand River to the west; the Bahmanshir River to the east; and the Karoon River to the north (Fig. 1). The Karoon River, with a length of

approximately 890 km and a catchment area covering around 60,000 km^2, is recognized as both the largest and the only navigable watercourse in Iran. The Karoon River flows through the Khuzestan plain, forming the Bahmanshir River before converging with the Arvand River (Fig. 1). The Bahmanshir River, extending approximately 83 km, runs through the northern and eastern edges of Abadan City, ultimately debouches into the Persian Gulf. The Arvand River serves as the expansive boundary between Iraq and Iran and holds the distinction of being the largest river in the Persian Gulf as it carries the combined flow of the Euphrates and Tigris Rivers, which join forming the Arvand River roughly 70 km northwest of Abadan city. The Arvand River flows through three majors two cities, namely Al-Basre in Iraq and Abadan in Iran. For the inhabitants of these cities, the Arvand River serves as a vital source of seafood and drinking water. Its formation occurs at the convergence of the Shatt al-Arab in Iraq and the Karoon River in Iran. The Persian Gulf receives an annual discharge of approximately 48 tons of oil residues from the Arvand River. (Hosseini et al. 2013).

Fig 1. Location of the Abadan freshwater resources and sampling sites

2.2. Sample collection and chemical analysis

A total of eight sampling sites were established in March 2023, which included one sample taken from the Karoon River (S1), two samples from the Bahmanshir River (S3 and S7), and five samples from the Arvand River (S2, S4, S5, S6, and S8). We selected these sampling sites so that they represent Abadan freshwater resources covering three rivers and all potential sources of PAHs. For each sampling location, the samples were collected in triplicate from three sub-sites, specifically from the river banks and middle of the channel, and combined to create a composite sample. To collect the surface sediment samples, a stainless steel Van Veen grab sampler was used at a depth

of 10 cm. Every 0.5-kg sample was carefully placed into a pre-cleaned wide-mouth glass jar and kept in an ice bucket containing crushed ice until shipped back to the laboratory for further analysis.

All samples were analyzed for the 16 US EPA priority PAHs, including Naphthalene (Nap), Acenaphthene (Ace), Fluorene (Flu), Acenaphthylene (Acy), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Chrysene (Chr), Benzo[a]anthracene (BaA), Benzo[k]fluoranthene (BkF), Benzo[b]fluoranthene (BbF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DahA), Benzo[g,h,i]perylene (BghiP), and Indeno[123-cd]pyren (InP). PAHs were extracted from 10 g of each of the sediment samples that had been previously dried and homogenized using a Soxhlet extractor. The extraction process involved using 250 ml of a mixture of n-hexane and dichloromethane (DCM) for a duration of 8 hours. Five surrogate internal standards including naphthalene-d8, phenanthrene-d10, p-terphenyl-d14, chrysene-d12, and perylene-d12 were directly added to the samples, prior to extraction. Elemental sulfur removal was carried out by treating the extracted samples with activated copper. Following this, they were concentrated and solvent-exchanged to n-hexane. Finally, the samples were further reduced to a volume of 2-3 mL using a rotary evaporator. For cleaning up the extracts, a 1:2 (v/v) alumina/silica gel column was utilized. The extracts were subjected to a 48-hour extraction process with DCM, followed by drying in a muffle furnace at temperatures of 180 °C and 240 °C for 12 hours. Then, PAHs were eluted with 70 mL of DCM/hexane (2:3). The eluate was reduced to 0.2 mL under a gentle gas stream consisting of pure nitrogen. To enable instrumental quantitation of the PAHs, a known quantity of hexamethylbenzene was added as an internal standard for PAH analysis. Gas chromatography–mass spectrometry (GC-MS) (Agilent 6890N/5975 MSD), coupled with an HP-5972 mass selective detector operating in the electron impact mode (70 eV), and equipped with a

DB-5 capillary column (30 m × 0.25 mm diameter, 0.25 μm film thickness) was employed. The GC carrier gas used was high-purity helium, flowing at a constant rate of 1.5 mL/min. The chromatographic parameters were set as follows: injector temperature at 270 °C, detector temperature at 280 °C, and oven temperature initially at 60 °C for 5 minutes, gradually increased to 290 °C at a rate of 3 °C min^{-1}, and then held for 40 minutes (Xing et al. 2011; Yang et al. 2013) . The identification of the target compounds was accomplished by analyzing the mass spectra and retention time. To ensure the precision and accuracy of the analytical methods, the recovery of surrogate standards was monitored. The percentage recoveries of the samples varied from 93% to 104%.

2.3. Potential ecological risk of PAHs

To assess the potential ecological risk of PAHs in sediment, measured concentrations were compared to the Effects Range Low (ERL) and Effects Range Median (ERM) standards proposed by Long and Macdonald (1998). Organisms' responses to PAHs are categorized based on their concentrations compared to the ERL and ERM benchmarks. Concentrations below the ERL are expected to be non-dangerous, concentrations above the ERM are identified as frequently dangerous, and concentrations between these benchmarks are considered harmful occasionally for organisms (Zhang et al. 2016; Haghnazar et al. 2023a). As single guideline values do not consider the toxic effects of mixtures of environmental contaminants, a mean ERM quotient (M-ERM-Q) was determined to estimate the ecological risk posed by the multiple toxic PAH components:

$$M-ERM-Q=\frac{\sum_{i=1}^{i=n} C_{sample}/ERM_i}{n} \quad (1)$$

in which C_{sample} is the concentration of PAH_i in the sediment, ERM_i is the value of ERM for the same PAH, i , and n refers to the number of PAHs in the study. The M-ERM-Q is classified into four levels with different ranges. The first level, ≤ 0.10, indicates no harmful biological effect. The second level, 0.11–0.50, suggests a potential adverse effect. The third level, 0.51–1.50, signifies a moderate adverse effect. Finally, the fourth level, > 1.50, represents a significant harmful effect (Lin et al. 2018).

Among all 16 PAHs, seven PAHs including Chr, BaA, BbF, BkF, BaP, DahA, and InP are identified as potentially carcinogenic to humans (Miao et al. 2023). Specifically, BaP is recognized as one of the most hazardous PAHs, and it serves as a benchmark for assessing the relative toxicity of other PAH compounds (Thiombane et al. 2019). The sediment toxicity based on seven carcinogenic PAH (ΣC-PAHs) was determined by toxicity equivalency factors (TEFs). BaP was designated as the reference chemical with a value of 1, whereas other PAHs were assigned specific TEF values according to their relative carcinogenicity to BaP. The toxicity of sediments is calculated using the BaP toxic equivalent quantity (TEQ_{BaP}) as follows (Qu et al. 2018):

$$TEQ_{BaP} = \sum_{i=1}^{i=7} TEF_i \times C_{PAH_i} \quad (2)$$

in which TEQBaP, TEF, and C are the toxic equivalent quantity based on BaP, the toxicity equivalency factor for PAH_i, and the concentration of PHA_i, respectively. According to USEPA (2012), TEFs for Chr, BaA, BbF, BkF, BaP, DahA, and InP were 0.01, 0.1, 0.1, 0.1, 1, 5, and 0.1, respectively.

2.4. Potential human health risk of PAHs

The risk to human health resulting from PAH exposure was evaluated through the calculation of Incremental Lifetime Cancer Risk (ILCR). ILCR represents an individual's increased probability of developing cancer over their lifetime due to exposure to substances with carcinogenic potential (Han et al. 2022). Dermal contact is considered the primary pathway for PAH exposure in sediment. Additionally, unintentional ingestion of sediments, such as through hand-to-mouth intake could also contribute to exposure (Ashayeri et al. 2018; Ghasemi and Keshavarzifard, 2022). The ILCR due to ingestion and dermal contact are calculated using the following equations (Chen et al. 2022):

$$ILCR_{ing} = \frac{TEQ_{BaP} \times CSF_{ing} \times \sqrt[3]{BW/70} \times IR_{ing} \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

$$ILCR_{derm} = \frac{TEQ_{BaP} \times CSF_{derm} \times \sqrt[3]{BW/70} \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (4)$$

$$ILCR_{total} = ILCR_{ing} + ILCR_{derm} \quad (5)$$

where TEQ_{BaP} is the toxic equivalent quantity based on BaP, CSF_{ing} and CSF_{derm} are the carcinogenic slope factor for ingestion and dermal contact, respectively (mg/kg/day) (Chen et al. 2022); BW is the average body weight, 70 kg for adults and 15 kg for children (USEPA, 2014); IR_{ing} is the sediment ingestion rate for receptor, 100 (mg/day) for adults and 200 (mg/day) for children (Grmasha et al. 2023); EF is the exposure frequency, 350 (days/year) for both adults and children (USEPA, 2014); ED is the exposure duration, 20 years for adults and 6 years for children (USEPA, 2014); CF is the conversion factor, 10^{-6} for both adults and children; AT is the averaging time for carcinogenic effects, 70 × 365 = 2550 (days) for both adults and children (Grmasha et al. 2023); SA is the skin surface area, 5700 (cm^2/day) for adults and 2800 (cm^2/day) for children

(USEPA, 2014); AF is the sediment to skin adherence factor, 0.07 (mg/cm^2) for adults and 0.2 (mg/cm^2) for children (USEPA, 2011); and ABS is the dermal absorption factor for PAHs, 0.13 for both adults and children (USEPA, 2011). $ILCR_{total}$ values below 10^{-6} indicate a complete absence of risk, values between 10^{-6} and 10^{-4} suggest an acceptable level of carcinogenic risk, and $ILCR_{tota}$ values exceeding 10^{-4} present a risk of cancer.

3. Results and discussion

3.1. Concentration, spatial distribution, and composition of PAHs in the surficial sediments

Descriptive statistical data and spatial distribution of 16 PAHs in the surficial sediments of Karoon, Bahmanshir, and Arvand rivers are presented in Table 1 and Fig. 2, respectively. The total PAHs concentration ranged from 67.8 to 57743 ng/g with an average of 8222 ng/g. Lower molecular weight PAHs (composed of two to three rings) had a mean concentration of 4673 ng/g, whereas higher molecular weight PAHs (with four to six rings) had a mean concentration of 3549 ng/g. Flu exhibited the highest mean concentration among the PAHs at 1177 ng/g, followed by Phe, Chr, and Acy with mean concentrations of 974, 959, and 839 ng/g, respectively. On the contrary, BbF had the minimum concentration in the sediments with a mean concentration of 46.4 ng/g. The concentrations of ΣC-PAHs ranged from 18 to 16104 ng/g, with a mean value of 2349.4 ng/g. These seven carcinogenic PAHs accounted for approximately 30% of all the PAHs in the sediment, emphasizing the significant presence of carcinogenic compounds. The total concentration of PAHs in sampling sites ranked in the order of S5 (55679 ng/g) > S1 (2374.9 ng/g) > S4 (1970.6 ng/g) > S6 (1963.2 ng/g) > S8 (743.8 ng/g) > S2 (596 ng/g) > S3 (196.8 ng/g) > S7 (97.2 ng/g).

Table 1. The concentration of PAHs (ng/g) in sediments samples collected from the Abadan water resources.

The highest concentration of ∑PAHs was found in sampling site S5, which is close to the Abadan oil refinery. The high concentration of PAHs in this sampling site is due to petrogenic contamination associated with the discharge of petroleum emission and leakage into the Arvand River. The concentration of PAHs in this sampling sites ranged from 165 to 8994 ng/g with the order of Flu > Chr > Phe > Acy > Ace > Nap > Pyr > Ant > DahA > BghiP > BaA > BkF > InP > BaP > Fla > BbF. Other highly concentrated areas were found in sampling sites S1, S4, and S6, which are related to effluents from a soap factory, a petrochemical complex, and downstream of Abadan oil refinery, respectively. According to the concentration ranges, the pollution levels of total PAHs can be classified into four categories: low pollution (<100 ng/g), moderate pollution (101-1000 ng/g), high pollution (1001-5000 ng/g), and very high pollution (>5000 ng/g) (Bemanikharanagh et al., 2017). Using this criterion, sampling site S7 was identified as having low pollution levels, sampling sites S2, S3, and S8 were found as moderately polluted, sampling sites S1, S4, and S6 were classified as highly polluted, and sampling site S5 was determined to be very highly polluted site.

Fig. 2. Spatial distribution of PAHs in the surficial sediments

Figure 3 illustrates the distribution of PAHs in the sediments, categorized according to the number of aromatic rings. PAHs can be classified into five groups, namely 2-, 3-, 4-, 5-, and 6-ring PAHs, and the percentages of these different PAH types are displayed in Fig. 3. According to Fig. 3, a larger fraction of total PAHs was composed of by 3- and 4-ring compounds (77.1%). The Abadan oil refinery sampling site (S5) exhibited a higher percentage (53%) of 3-ring PHAs, which can be

attributed to sediment pollution caused by petrogenic PAHs due to petroleum emission and leakage. On the other hand, the sampling site S1 had a higher percentage (43%) of 4-ring PAHs. This increase is likely associated with the soap-making processes at the factory.

Fig. 3. Composition profile of total PAHs in sampling sites

3.2. Sources of PAHs in the surficial sediments

PAHs can originate from four main sources: geogenic, petrogenic, pyrolytic, and biogenic (Traven, 2013). Diagnostic ratios are widely employed to determine the potential sources of PAH contamination in the environment (Wu et al. 2019; Ambade et al. 2023). These ratios, such as Ant/(Ant + Phe), Fla/(Fla + Pyr), BaA/(BaA + Chr), and InP/(InP + BghiP), have been extensively used to investigate the origins of PAHs. The Ant/(Ant + Phe) ratio is particularly useful for identifying petrogenic sources, whereas the Fla/(Fla + Pyr), BaA/(BaA + Chr), and InP/(InP + BghiP) ratios are more effective in identifying pyrolytic sources. According to Yunker et al. (2022), if the Ant/(Ant + Phe) ratio is less than 0.1, it indicates petroleum contamination as the source; otherwise, biomass and coal combustion are the likely sources. A Fla/(Fla + Pyr) ratio of less than 0.4 suggests petroleum sources, whereas a ratio greater than 0.5 indicates biomass and coal combustion. Otherwise, petroleum combustion, including gasoline, kerosene, and crude oil, is the probable source. If the BaA/(BaA + Chr) ratio is below 0.2, it suggests that petroleum emissions are the main contributor to PAH pollution. On the other hand, a ratio exceeding 0.35 indicates that biomass and coal combustion are the predominant sources. When the ratio falls between these two

values, it signifies petroleum combustion pollution. Finally, ratios of InP/(InP + BghiP) less than 0.2, greater than 0.5, and between 0.2 and 0.5 show petroleum, biomass and coal combustion, and petroleum combustion, respectively, as the sources of PAHs. As shown in Fig. 4, At all the sampling sites, the Ant/(Ant + Phe) ratio exceeded 0.1, suggesting the presence of biomass and coal combustion as a likely source of PAHs.

Fig. 4. Diagnostic ratios for source analysis

Regarding the Fla/(Fla + Pyr) ratio, sampling sites S3, S4, S5, S6 and S8 exhibited values ranging from 0.13 to 0.37, indicating potential emissions from petroleum sources. In contrast, at sampling sites S2 and S7, the PAHs may originate from petroleum combustion, as the Fla/(Fla + Pyr) ratios fell between 0.4 and 0.5. At sampling site S1, the ratio of Fla/(Fla + Pyr) exceeded 0.5, indicating a source related to biomass and coal combustion. The BaA/(BaA + Chr) ratios varied from 0.18 to 0.83, suggesting the presence of three different sources of PAHs. Sampling site S5 exhibited a ratio below 0.2, suggesting petroleum as a source, whereas sampling site S1 demonstrated a ratio exceeding 0.35, indicating biomass and coal combustion. The ratios at sampling sites S2, S3, S4, S6, S7, and S8 fell within the 0.2 to 0.35 range, indicating petroleum combustion. Finally, the InP/(InP + BghiP) ratios for all sampling sites ranged from 0.2 to 0.5, signifying petroleum combustion as a major source of PAHs in the study area.

Additionally, principal components analysis (PCA) was employed to identify the potential sources of PAHs in the surficial sediments of the Abadan water resources (Agyeman et al. 2023; Şimşek et al. 2023; Haghnazar et al. 2023b). The result of PCA with eigenvalues > 1 is given in Fig. 5. Two principal components were extracted in the sediments, describing 94.4% of the total variance. The first component (PC1) explained 71.9% of the total variance and was specified by Ace, Acy,

Fla, Pyr, BaA, BbF, BkF, BaP, DahA, BghiP, and InP. The presence of BaP, BghiP, and InP might be an indicator of diesel and gasoline combustion. (Motelay-Massei et al. 2005; Araki et al. 2009; Montuori et al., 2016).

Fig 5. Loading factors of PCA for the surficial sediments

In addition, BbF, BkF, and DahA are indicators of petrol combustion, particularly diesel combustion (Larsen and Baker, 2003). As a result, PAHs containing 5-6 rings primarily originate from automobile exhaust emissions. Pry, BaA, and Fla are indicators of coal combustion and diesel emission sources (Yang et al. 2013). Ace and Acy are the main products of coal and biomass combustion (Simcik et al. 1999; Wang et al, 2013). Overall, the first principal component represents a source related to traffic, coal, and biomass combustion sources. The second component (PC2) is comprised of Nap, Flu, Phe, Ant, Chr, BaA, and BaP with 22.5% of the total variance. The main source of Nap is predominantly attributed to oil-related factors, which encompass oil leakage and the release of by-products throughout the production and transportation processes (Shi et al. 2022). Flu, Phe, and Ant are also associated with petrogenic sources (Pampanin and Sydnes 2013). In addition, Nap, Flu, and Phe, BaA are commonly detected in the discharge from industries and municipal wastewater (Guo et al. 2007; Gaurav et al. 2021). Overall, the second principal component is associated with petroleum leakage and wastewater.

3.3. Ecotoxicological concerns and cancer risk

The concentration of PAHs at the sampling sites was compared to the respective ERL and ERM values. The findings revealed that except for Ace, Flu, and Acy, the levels of other PAHs were below their corresponding ERL values at sampling sites S1, S2, S4, and S6. Moreover, the concentration of DahA at sampling sites S1 and Phe at sampling sites S4 and S6 exceeded their

corresponding ERL values. At sampling sites S3, S7, and S8, all PAH concentrations were detected below the ERL values, except for Flu and Ace at Sampling site S8. Conversely, at sampling site 5, all PAH concentrations were higher than the ERL values, except for BbF. Additionally, Nap, Ace, Flu, Acy, Phe, Ant, Pyr, Chr, DahA, BghiP, and InP concentrations surpassed their corresponding ERM values. Overall, the results indicate that the presence of PAHs in the sediments of the Bahmanshir River is unlikely to cause adverse biological effects. Occasionally, adverse biological effects were observed downstream of the Karoon River, and damage to the biota was found in the Arvand River. We also calculated the M-ERM-Q values to determine the toxicity of PAHs in the sediment samples. The values of M-ERM-Q at sampling sites ranked in the order of S5 (3.99) > S1 (0.13) > S6 (0.11) > S4 (0.09) > S2 = S8 (0.03) > S3 (0.01) > S7 (0.006). According to the values of M-ERM-Q, a substantial harmful effect for organisms was detected for sampling site S5 (high ecological risk). Sampling sites S1 and S6 indicated a potential adverse effect (medium-low ecological risk), however, no harmful biological effect (low ecological risk) was found in sampling sites S2, S3, S4, S7, and S8. We also analyzed the values of TEQBaP for the sediments of the Abadan freshwater resources. The values of TEQBaP in sampling sites varied from 16 to 12424ng/g. Among all sampling sites, the highest values of TEQBaP were detected in S5 (12424.1 ng/g) followed by S1(904 ng/g), and then S6 (701ng/g). Sampling sites S7 and S3 had the lowest values of TEQBaP accounting for 65and 16 (ng/g), respectively. Based on Canadian guidelines for soil quality, it is recommended that the TEQBaP value should not exceed 600 ng/g for both ecosystem and human health protection (Yu et al. 2015). In the study area, the values of TEQBaP for sampling sites S5, S1, and S6 were detected as higher than the permissible values, indicating toxicity of the surficial sediments in these areas. This observation suggests that the presence of industrial effluents discharged by factories, municipal wastewater, and petroleum pollution

contribute substantially to the toxicity levels affecting human health and aquatic organisms within the study region.

A cancer risk assessment was conducted on the PAHs present in sediments of the Abadan freshwater resources, taking into account two main routes of exposure: ingestion and dermal absorption. The assessment encompassed both children and adults. The evaluation involved determining the toxic equivalency concentration TEQ found in the sediments. The TEQ value was assessed using the total BaPeq, which was calculated by applying toxic equivalence factors (TEFs) to each PAH. The findings indicated that children had higher ILCR values than adults through the two primary pathways. Among these pathways, the dermal absorption of sediments was identified as the primary route of exposure for PAHs, followed by ingestion for both adults and children. According to Table 2, the ranking of ILCR values across sampling sites was as follows: S5 < S1 < S6 < S4 < S8 < S2 < S7 < S3, applicable to both adults and children. It was observed that the calculated cancer risk values for all sampling sites exceeded the acceptable threshold of 1×10^{-4} for both adults and children. Consequently, the exposure to PAHs in Abadan freshwater resources posed a significant health risk in terms of cancer risk for both adults and children. Notably, although the ecological risk in the Bahmanshir River (sampling sites S3 and S7) was assessed as low, a substantial cancer risk was identified in this river. Overall, It is essential to mitigate the toxic and unintended consequences of PAHs on the river's ecological environment while also minimizing the potential risks to the health of nearby residents.

Table 2: ILCR values for adults and children exposed to sediments of the Abadan water resources.

4. Conclusion

The present study evaluated the distribution, potential sources, and ecological/human risks assessment of PAHs in the surficial sediments from the Karoon, Bahmanshir, and Arvand rivers in the Abadan freshwater resources, of the southwestern Persian Gulf. The results indicate that the rivers are subjected to significant PAH pollution, with concentrations ranging from 67.8 to 57,748 ng/g, with an average concentration of 8,222 ng/g. The presence of carcinogenic PAHs accounted for approximately 30% of all PAHs, indicating the presence of harmful compounds. The dominant PAHs in the sediments were 3- and 4-ring compounds, accounting for approximately 77.1% of the total PAHs. The Abadan oil refinery sampling site (S5) exhibited a higher percentage (53%) of 3-ring PAHs, indicative of sediment pollution primarily caused by petrogenic PAHs. Furthermore, diagnostic ratios and principal component analysis (PCA) indicated that biomass and coal combustion, petroleum sources, and wastewater were the primary contributors to PAH pollution in the study area. The highest concentration of PAHs was found in sampling site S5, suggesting the influence of petrogenic contamination from petroleum emission and leakage. Additionally, sampling sites S1, S4, and S6 exhibited high concentrations of PAHs, associated with effluents from a soap factory, petroleum products, and downstream of the oil refinery, respectively. Although some sampling sites showed concentrations below ecological risk limits, adverse biological effects were observed downstream of the Karoon River and in the Arvand River. Comparison of PAHs concentration with cancer risk limits revealed concerning findings. Specifically, the cancer risk assessment indicated that exposure to PAHs through ingestion and dermal absorption poses significant cancer risk for both adults and children in the region. Overall, the study area faces with high level of pollution with PAHs and remedial actions are necessary. Effective regulatory measures and management strategies should be implemented to control PAH pollution and safeguard the Abadan freshwater resources and consequently the Persian Gulf. Efforts should focus on reducing emissions from oil refinery/petrochemical/industrial activities, improving wastewater

treatment processes, and implementing preventive measures to minimize the potential risks to human health and the ecological environment.

Acknowledgements

The authors are deeply thankful to the Research Center for Environmental Contaminants, Abadan University of Medical Science for providing the financial support (grant NO. IR.ABADANUMS.REC.1402.030) to conduct this research.

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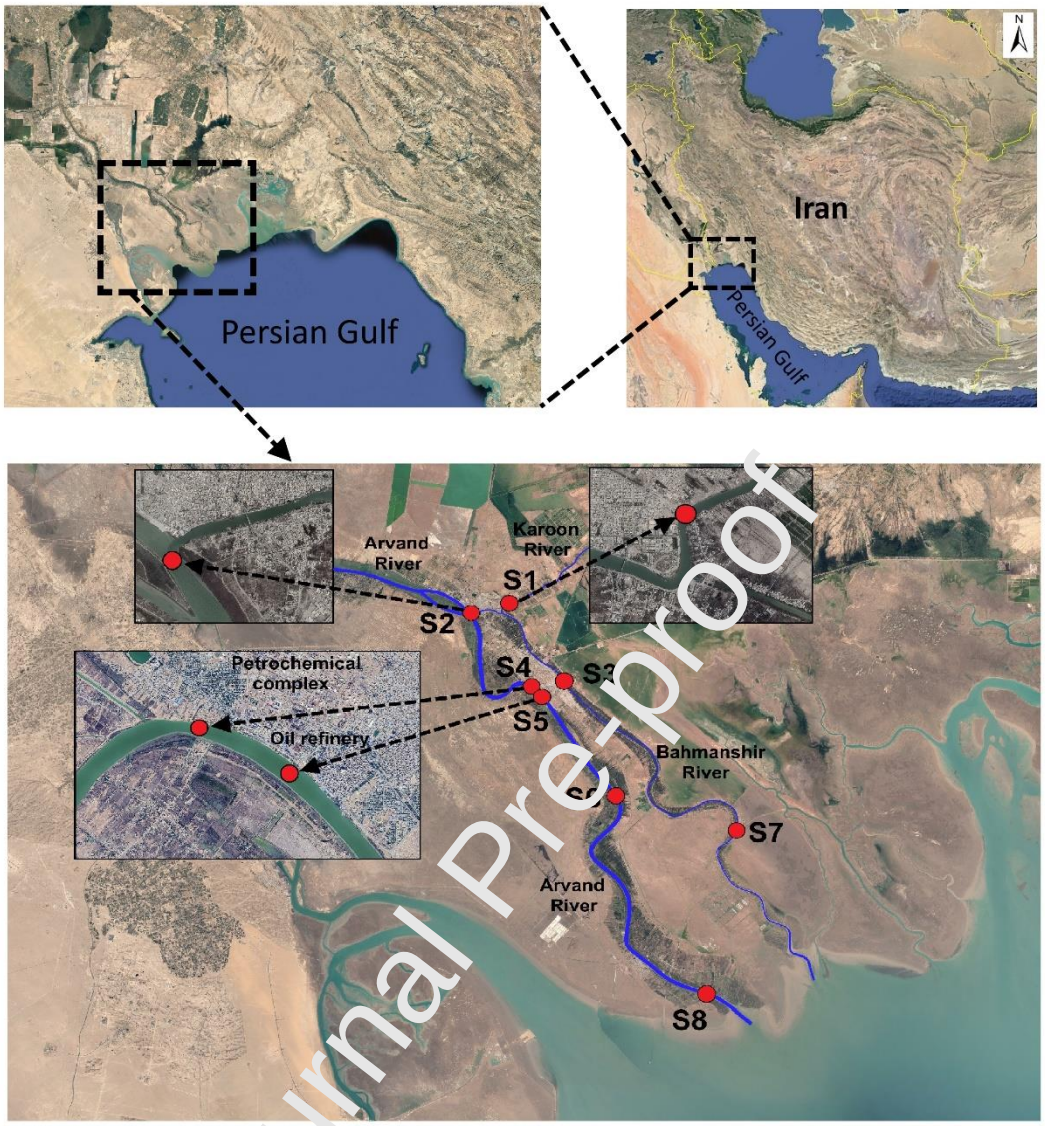


Fig 1. Location of the Abadan freshwater resources and sampling sites

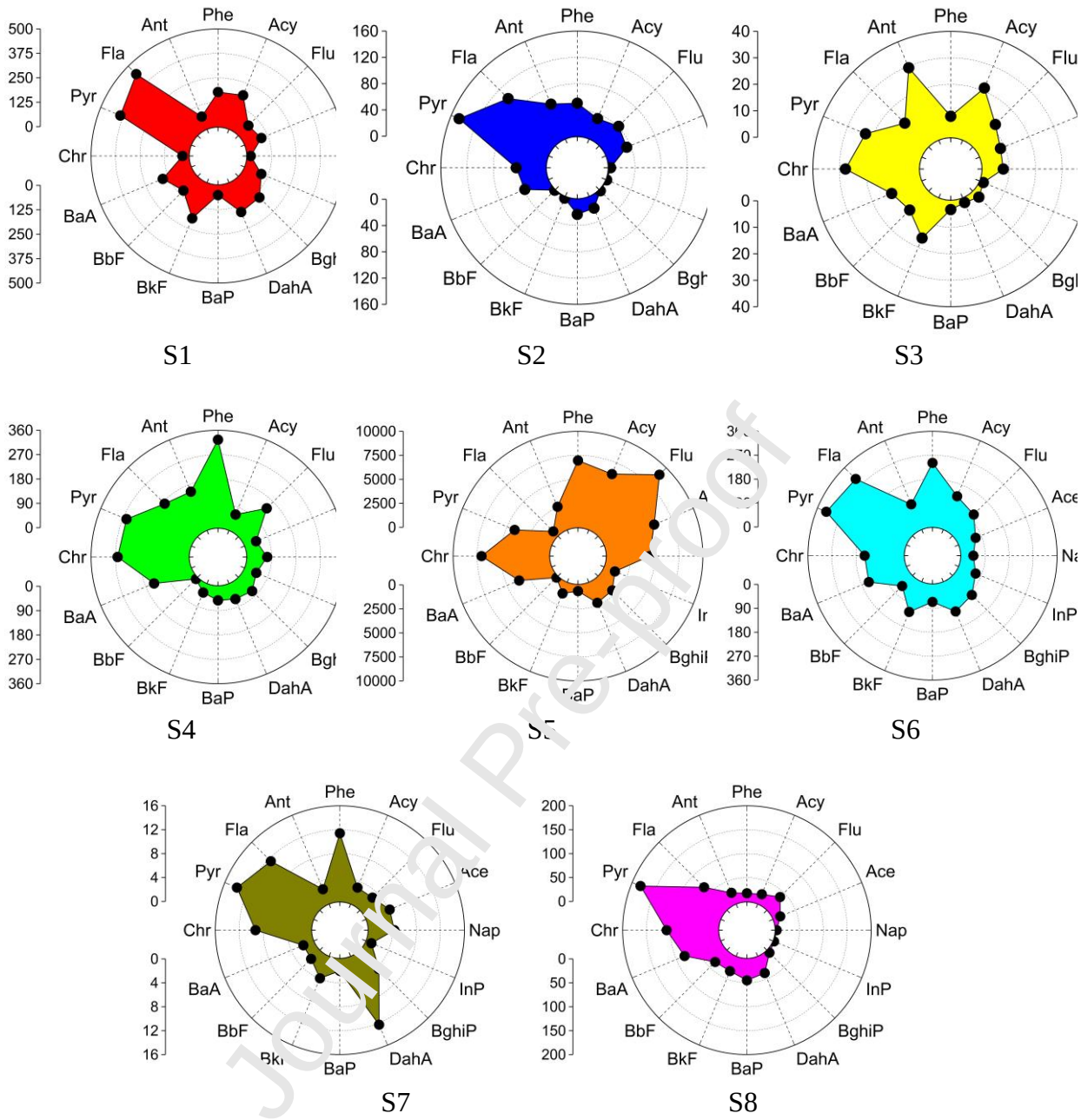


Fig. 2. Spatial distribution of PAHs in the surficial sediments

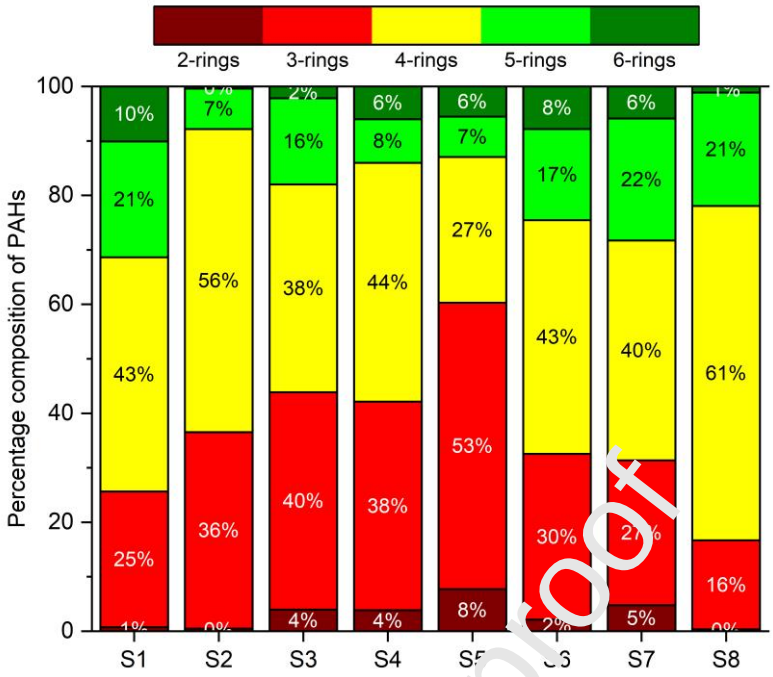


Fig. 3. Composition profile of total PAHs in sampling sites

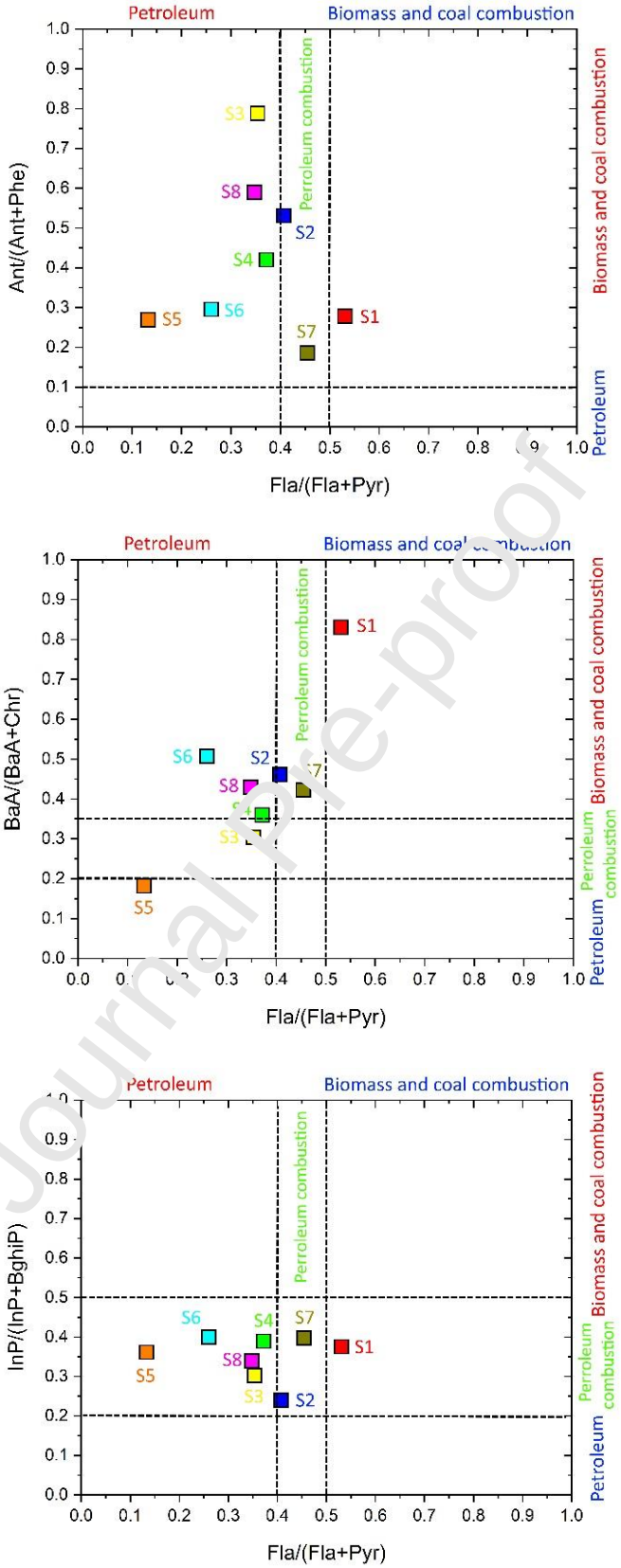


Fig. 4. Diagnostic ratios for source analysis

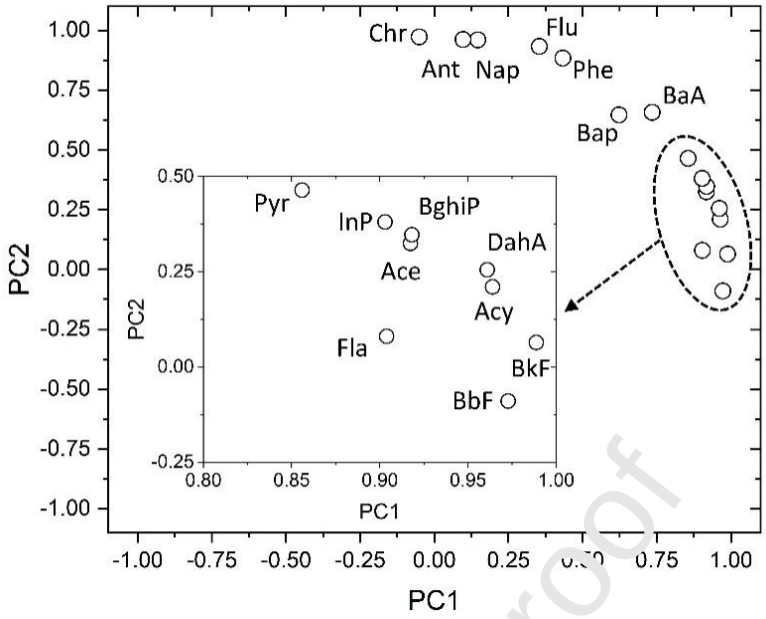


Fig 5. Loading factors of PCA for the surficial sediments

Table 1. The concentration of PAHs (ng/g) in sediments samples collected from the Abadan water resources.

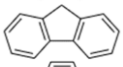
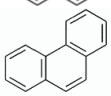
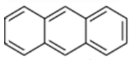
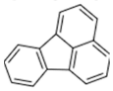
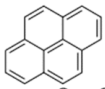
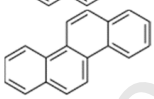
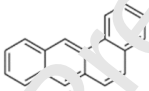
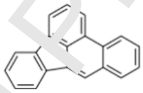
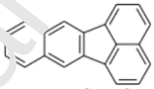
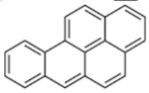
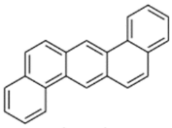
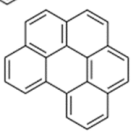
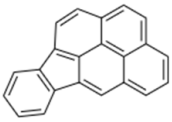
PAHs category	No. of rings	PAHs	Chemical Structure	Min	Max	Mean	SD	ERL-ERM
LMW PAHs	2	Nap		2.32	4455	576	1567	160 - 2100
	3	Ace		4.2	5586	731	1962	44 - 640
	3	Flu		2.9	8994	1177	3159	19 - 540
	3	Acy		2.9	6251	839	2188	16 - 500
	3	Phe		7.9	6963	974	2423	240 - 1500
	3	Ant		2.6	25[illegible]9	376	885	853 - 1100
HMW PAHs	4	Fla		11.5	[illegible]34	217	223	600 - 5100
	4	Pyr		1[illegible]8	4142	685	1403	665 - 2600
	4	Chr		[illegible]3	7043	959	2459	384 - 2800
	4	BaA		1.8	3632	527	526	261 - 1600
	5	BbF		0.5	165	46.4	58.7	320 - 1880
	5	BkF		2.15	1200	201	409	280 - 1620
	5	BaP		2	645	111	217	430 - 1600
	5	DahA		1.7	2260	334	780	63.4 - 260
	6	BghiP		1.75	2050	298	710	430 - 1600
	6	InP		0.55	1159	171	400	160 - 2100
∑LMW PAHs	–	–	–	22.8	34818	4673	–	–
∑HMW PAHs	–	–	–	45.1	22930	3549	–	–
∑16PAHs	–	–	–	67.8	57748	8222	–	–

Table 2: ILCR values for adults and children exposed to sediments of the Abadan water resources.

Sample	Adults			Children		
	Ingestion	Dermal	Total	Ingestion	Dermal	Total

1	2.58E-03	4.59E-03	7.17E-03	4.33E-03	5.40E-03	9.72E-03
2	3.45E-04	6.13E-04	9.58E-04	5.78E-04	7.20E-04	1.30E-03
3	4.58E-05	8.13E-05	1.27E-04	7.67E-05	9.56E-05	1.72E-04
4	1.08E-03	1.92E-03	3.00E-03	1.81E-03	2.26E-03	4.06E-03
5	3.55E-02	6.31E-02	9.86E-02	5.95E-02	7.41E-02	1.34E-01
6	2.00E-03	3.56E-03	5.57E-03	3.36E-03	4.19E-03	7.55E-03
7	1.86E-04	3.31E-04	5.17E-04	3.12E-04	3.89E-04	7.01E-04
8	7.03E-04	1.25E-03	1.95E-03	1.18E-03	1.47E-03	2.65E-03

Author contributions

All authors contributed to the study conception and design.

Hamed Haghnazar: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Visualization.

Yasaman Abbasi & Reza Morovati: Conceptualization, Methodology, Formal analysis.

Renato Somma: Conceptualization, Methodology.

Karen H. Johannesson: Supervision, Conceptualization, Methodology, Writing - Review & Editing.

Mojtaba Pourakbar: Resources, Investigation.

Ehsan Aghayani: Funding acquisition, Resources, Investigation.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights:

1- PAHs assessment showed high/very high pollution due to petrogenic and industrial contamination

2- Biomass and coal combustion, petroleum emissions, and traffic were as the major sources of PAHs.

3- Potential harm to aquatic organisms, particularly in highly polluted areas was identified.

4- Significant health risks for both adults and children exposed to PAHs were detected.