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Published Version

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Abdulla, M. A., Castillo, A. B., Collins, C. and Sizmur, T.  
ORCID: <https://orcid.org/0000-0001-9835-7195> (2023)  
Ecological indicators and source diagnostic ratios of aliphatic  
and polyaromatic hydrocarbons in marine sediments of Qatar.  
Regional Studies in Marine Science, 64. 103042. ISSN 2352-  
4855 doi: 10.1016/j.rsma.2023.103042 Available at  
<https://centaur.reading.ac.uk/112272/>

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To link to this article DOI: <http://dx.doi.org/10.1016/j.rsma.2023.103042>

Publisher: Elsevier

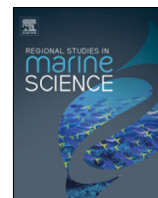
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# Ecological indicators and source diagnostic ratios of aliphatic and polyaromatic hydrocarbons in marine sediments of Qatar

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## ARTICLE INFO

### Article history:

Received 16 February 2023

Received in revised form 30 May 2023

Accepted 3 June 2023

Available online 7 June 2023

### Keywords:

Petroleum hydrocarbons

Aliphatic hydrocarbons

Polycyclic aromatic hydrocarbons

Diagnostic ratio

Ecological assessment

## ABSTRACT

The marine ecosystems surrounding oil and gas production sites are particularly vulnerable to ecological harm that may be affected by its operations. In this study, we examined the composition, contaminant sources, and the potential ecological risk of aliphatic hydrocarbons (AH) and polyaromatic hydrocarbons (PAH) in the marine sediments along the western coast of Qatar. The  $\Sigma$ AHs concentration ranged from  $<0.10$  to  $246 \text{ ng}\cdot\text{g}^{-1}$  (site SD2) while the  $\Sigma$ PAH concentration ranged from  $<0.10$  to  $44 \text{ ng}\cdot\text{g}^{-1}$  (site SD10). Pollution concentration profile was site specific where AH and PAH concentrations were relatively higher within close proximity to the oil and gas production. TOC appeared to be positively correlated with PAH and therefore a good indicator for PAH but not for AH. Low molecular weight even-carbon numbered alkanes ( $n$ -C10–18) were more abundant than the higher molecular weight ( $n$ -C20–34) AHs. The  $\Sigma$ 16PAHs compositional analysis mean concentrations were composed of 2-ring (6%), 3-ring (18%), 4-ring (48%), 5-ring (28%), and 6-ring (0.14%), respectively. Fluoranthene obtained the highest concentration of  $11 \text{ ng}\cdot\text{g}^{-1}$  (site SD10). Diagnostic ratios and hydrocarbon parameters suggested mixed sources of petrogenic, pyrolytic, and biomass except for vehicular traffic. The overall results for AH and PAH indicated low pollution based on pollution criteria and were below the threshold limit set by the National Oceanic and Atmospheric Administration (NOAA) and the Canadian Sediment Quality Guidelines (CSQG). This suggests low probability of a negative toxic effect caused by these contaminants however, continuous long term-monitoring is needed to ensure these pollutants do not exceed the current levels.

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## 1. Introduction

Petroleum occurs naturally as complex mixtures of carbon, hydrogen and other elements such as oxygen, nitrogen and sulfur. Total petroleum hydrocarbon is a term used to describe petroleum-based hydrocarbons that are found in crude oil, which can be measured in environmental media. It includes both volatile and extractable petroleum hydrocarbons such as crude oil, diesel fuels, jet fuels, gasoline, kerosene, Stoddard solvent, fuel oils No. 5 and 6, mineral-based motor oils, hexane, benzene, toluene, xylenes, and polyaromatic hydrocarbons (PAHs). Petroleum hydrocarbons are ubiquitous organic contaminants in coastal areas and can broadly be classified into aliphatic and aromatic hydrocarbons, which may be derived from biogenic, petrogenic and pyrolytic sources (Seopela et al., 2020). Petroleum hydrocarbons

undergo considerable changes in their composition once entering into the sea due to evaporation, photo and chemical oxidation, biodegradation, and selective dissolution. Short chain alkanes and aromatics with few carbon rings are lost rapidly, while complex aromatic molecules are more stable and can be used to attribute the source of contamination (Kucuksezgin et al., 2012).

Hydrophobic compounds are mostly deposited into the marine sediment through association with solid particulate matter (Wang et al., 2015a). As a result of their low degradation and high affinity to sediment particles, they have low bioavailability, but persist in the marine ecosystem. Sources of hydrocarbons in sediments vary in their origin but may include incomplete combustion of fossil fuels, hydrocarbons biosynthesis by terrigenous or marine organisms, and different petroleum operations related to oil field industry i.e., drilling, extraction, transportation, accidental spillage, and leakage of oil and gas (Kucuksezgin et al., 2012). Assessment of aliphatic hydrocarbons (AHs) and polyaromatic hydrocarbons (PAHs) concentrations in coastal sediments provides an insight into their distribution and can highlight hotspots of contamination associated with petroleum production (Sammarco et al., 2013).

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In the marine environment, the hydrocarbons of the petroleum oil spilled are mixed with the pre-existing organic hydrocarbons in the sea mainly originating from biogenic activities or natural sources. In addition, petroleum hydrocarbons are lipophilic substances, which promote bioaccumulation in marine food chain. Research has shown that petroleum hydrocarbons are easily absorbed in the gastrointestinal tract (Gupta, 2016). Gupta (2016) revealed that aliphatic hydrocarbons were associated with accidental poisoning among children which resulted to 12%–25% deaths from the 28,000 children under 5 years of age who had been reported to have ingested petroleum distillates. It is therefore crucial to explore the origin of hydrocarbons in the marine environment to determine the contribution of each part, evaluate their potential risk, and formulate control measures.

Qatar in a peninsula within the Arabian Gulf which represents about 23% of the entire Gulf coastline and supports a range of marine ecosystems including coral reefs, sand and mud flats, mangrove swamps and seagrass beds, in addition to high fish diversity (Walton et al., 2017). It is also one of the world's most important oil transit passages because of the large volume of petroleum oil and products that are transported through the strait (Barden, 2019). The crude petroleum and natural gas industry in Qatar accounts for over 50% of the gross domestic product and is the largest industry in the country (GPCA, 2015).

The present study area is located on the western coast of Qatar and is the site of a large oil and gas field producing crude oil, gas condensate, associated, and non-associated gas that covers an area approximately 80 km by 8 km since 1949 (QP, 2017). Due to these petroleum-related activities, the coastline is susceptible to petroleum-associated pollution and, because of the shallow water, the pollutants in this area are more likely to disperse slowly, partially dilute, and reside in the environment for long periods of time (De Mora et al., 2004). The main objective of this research is to quantify the aliphatic hydrocarbons and USEPA's 16 priority PAH pollutants across the west coast of Qatar. This study will also evaluate the interrelationship between the organic pollutant concentrations and the proximity to the oil and gas exploration and production activities. Lastly, the study will identify source-apportionment using diagnostic ratios and understand the potential ecological risks posed by these organic pollutants including comparison of their levels with the threshold effect limits set by the National Oceanic and Atmospheric Administration (NOAA) and the Canadian Sediment Quality Guidelines (CSQG).

## 2. Materials and methods

### 2.1. Study area and sampling

Marine sediments were sampled in May 2019 from 22 sampling sites along a 10 km stretch of the western coast of Qatar in Dukhan (SD1 to SD20; group A); including two reference sites approximately 29 km to the north located in Zekreet (SZK, group B) and 24 km to the south located in Umm Bab (SUB, group C) (Fig. 1). Dukhan, a city in the western municipality of Al-Shahaniya, is the site of the first discovery of oil reserve in Qatar. The oil exploration in the area begun in 1935 and the construction of the first oil well was completed in 1940 (MOFA, 2012; Sorkhabi, 2010). Dukhan is administrated by Qatar Energy (formerly Qatar Petroleum) which is the country's state oil agency (QP, 2017). In 1949, the first barrel of oil was exported and since then Dukhan's development grew at a steady state especially when natural gas was found (MOFA, 2012). Dukhan's onshore field covered 605 hydrocarbon wells of which 300 were oil producing, 58 were gas producing and 182 were for other uses e.g., water injection wells (Sorkhabi, 2010; Offshore Technology, 2021). The onshore Dukhan field produces up to 335,000 barrels (53,300 m<sup>3</sup>) of crude oil per day which accounts for 5% of

the country's daily output (Sorkhabi, 2010; Offshore Technology, 2021).

A total of 66 samples were taken from the intertidal zone with approximately 500 m distance between each sampling site. The samples were taken randomly about 5–10 cm from the surface including three replicates using a trowel. The samples were homogenized removing any bulk particles or shells and placed in an acid washed 250 mL clear glass jar then transported to the Environmental Science Center laboratory (ISO17025 accredited) at Qatar University. The samples were stored in the freezer at −20 °C (ARCTIKO) then freeze-dried (Advantage Pro with Intellitronics-Vir Tis SP SCIENTIFIC) for 48 h prior to analysis. Physical parameters such as temperature and pH were measured *in situ* using a portable EXO3 Multiparameter Sonde-YSI calibrated with pH buffers 4, 7 and 10. The particle size distribution of sediments was analyzed using Mastersizer 3000, Malvern analyzer and classified according to the Gradistat Classification (Blott and Pye, 2001).

### 2.2. Analysis of PAHs and AHs

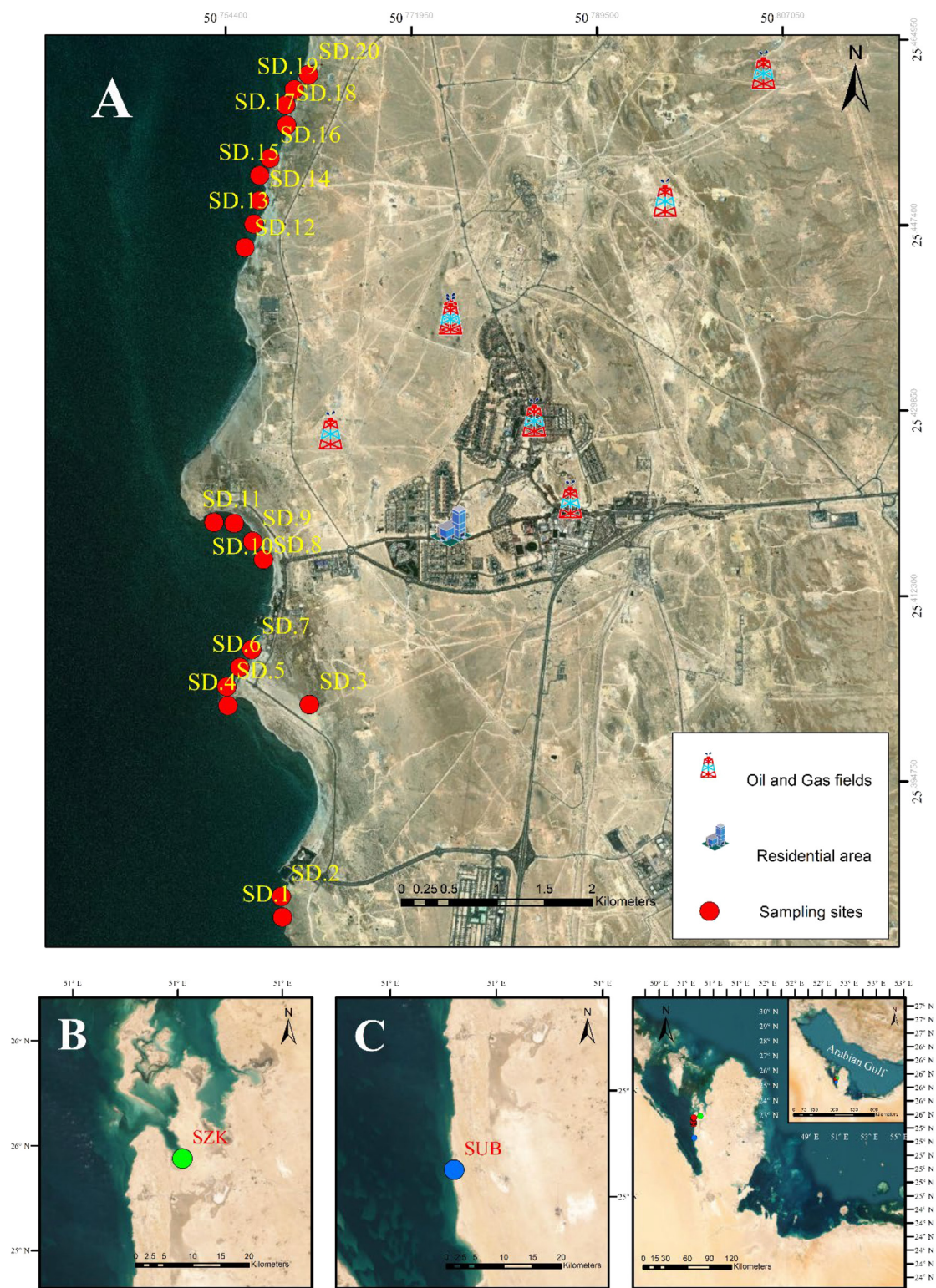
Approximately 10 g of freeze-dried sediment samples were analyzed for AHs and PAHs using USEPA 8015D and USEPA 8275A method (USEPA, 1996), respectively. The sediment samples were augmented with a diatomaceous earth filler and transferred into an extraction cell containing 20 g of pre-heated alumina. The extraction cells were then tightly sealed and placed into an accelerated solvent extractor (ASE 350, DIONEX) using dichloromethane at a temperature of 105 °C and a pressure of 10342 135.9 Pa. To elute the PAHs, the extract was cleaned using a 20 mL of dichloromethane in solid-phase extraction (SPE) cartridge. The eluted extract was collected in glass test tubes then subjected to further concentration down to 1 mL by evaporation (SE 500, DIONEX) using nitrogen gas. The 1 mL PAH extract was then transferred to a 2 mL amber injection vial then analyzed in Gas Chromatography Mass Spectrometry (GC-MS 7890A, Agilent). To elute the AHs, 20 mL of hexane was used, and similarly evaporated to 1 mL (SE 500, DIONEX) using nitrogen gas. The 1 mL AH extract was transferred to 2 mL transparent injection vial then analyzed in Gas Chromatography Flame Ionization Detector (GC-FID 6890, Agilent). The target analyte concentrations were reported as nanogram/gram (ng g<sup>−1</sup>) based on dry sediment weight.

There are sixteen priority list PAHs designated by the United States Environmental Protection Agency (USEPA) as High Priority Pollutants which include naphthalene (NaP), acenaphthylene (Acl), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indene(1,2,3,cd)pyrene (InP), dibenzo(a,h)anthracene (DahA) and benzo(g,h,i)perylene (BghiP). In this study, these PAH compounds are classified according to the number of rings whereby 2–3 ring PAHs are considered low molecular weight (LMW) PAHs, whereas the 4–6 ring PAHs are considered high molecular weight (HMW) PAHs. The 12 even-number (C10–C32) aliphatic hydrocarbon compounds are grouped according to C10–C18 as LMW AH, while C20–C32 as HMW AH.

### 2.3. Total organic carbon (TOC) analysis

TOC content in coastal sediment samples was calculated from the difference in concentration of total carbon (TC) and total inorganic carbon (TIC). The analysis was done using Primacs SNC100 SKALAR C/N analyzer by dry combustion method. For TC determination, approximately 75–80 mg of ground dry sediment





**Fig. 1.** Study area showing the 20 sampling points in Dukhan (A), and 2 reference points Zekreet (B) and Umm Bab (C).

samples was weighed into ceramic crucibles and combusted in pure oxygen at 1200 °C before the CO<sub>2</sub> was quantified using an infrared detector. For TIC analysis, about 25–30 mg of ground dry sediment samples were weighed into the glass test tubes. One mL of carbon-free water was then added, and the TIC content was determined via acidification using o-phosphoric acid and sparging

at 150 °C to liberate CO<sub>2</sub> from the carbonates and then quantified using an infrared detector.

#### 2.4. Quality control

Solvents, reagents, and chemicals used in this study were HPLC and Pesticide grade from Sigma-Aldrich and Honeywell.

For quality assurance, various quality control measures were performed using duplicates and control samples spiked with surrogate standards. Surrogate standards used was Method 252.2 Surrogate Standard Mix (CAS# 31826) from Restek with compounds Perylene-d12 and Pyrene-d10. Certified Reference Materials (CRMs) for marine sediment were also used for each analysis using SIGMA CRM 361 for AH and NIST SRM 1941b for PAHs. Satisfactory recoveries of  $\pm 15\%$  from the true value were obtained for the AH and PAHs. Limit of detection (LOD) of the instrument was 0.1 ng/g for AH and 0.1 ng/g for PAHs, and a  $< LOD$  was used to report the values. LOD was calculated from the 95% confidence interval of 10 replicates of the 5  $\mu\text{g/g}$  standard (Armbruster and Pry, 2008). The concentrations of TC and TIC were confirmed using a known standard of solid glycine (dried to constant weight, Sigma-Aldrich) and solid calcium carbonate (Sigma-Aldrich) respectively. The recovery obtained was in the range of  $98.45 \pm 0.34\%$  to  $100.91 \pm 0.21\%$ .

## 2.5. Statistical analysis

Analysis of Variance (ANOVA) was performed, followed by *posthoc* Tukey's HSD test, to identify significant differences in the concentrations of AH and PAH between sampling sites. Furthermore, Dunnett test was also performed to compare the sites in group A (SD 1–20) to the reference sites Zekreet, SZK (group B) and Umm-Bab, SUB (group C). All data were tested for homogeneity and normality, otherwise a non-parametric Kruskal-Wallis test and Bonferroni correction test were used. Pearson Correlation Coefficients were used to quantify the correlation between the studied variables and parameters. The relationships between variables, including levels of AH, PAHs, TOC, pH and temperature in coastal marine sediment, were explored using Principal Component Analysis (PCA).

## 2.6. Diagnostic ratios

### 2.6.1. LMW/ HMW index

In the presence of fresh crude oil, the ratio of the concentration of LMW (C10–C18) AH to the concentration of HMW (C20–C32) AH was used as indicator (Gearing et al., 1976; Rostami et al., 2019). Due to the presence of light and heavy hydrocarbons in the crude oils, this ratio is about 1 for the hydrocarbons originating from oil and is indicative of the higher concentrations of soluble aliphatic hydrocarbons in the sediment and fresh source of petroleum hydrocarbons (Gearing et al., 1976).

The concentrations and distribution pattern of PAHs analyzed in sediments had also been shown to reflect source characteristics (Seopela et al., 2020). LMW PAHs (2–3 rings) are usually an indication of petroleum contamination while the HMW PAHs (4–6 rings) are from pyrogenic source e.g., thermal combustion. The ratio of LMW/HMW PAHs  $< 1$  indicates sediment pollution by pyrolytic inputs while LMW/HMW PAHs  $> 1$  represents petrogenic sources of pollution (Baumard et al., 1998; Rostami et al., 2019).

### 2.6.2. The ratio of $\Sigma n$ -Alkanes/ $n$ -C16

The ratio of the concentration of all normal alkanes to the concentration of alkanes with 16 carbon atoms ( $\Sigma n$ -alkanes/ $n$ -C16) was determined for the sediment samples.  $\Sigma n$ -Alkanes/ $n$ -C16  $< 15$  indicates contamination of samples with crude oil, while  $\Sigma n$ -alkanes/ $n$ -C16  $> 50$  suggests hydrocarbon distribution of biological origin (Rostami et al., 2019).

### 2.6.3. PAH isomer diagnostic ratios

The use of diagnostic ratios uses the difference in isomer stability to investigate sources of PAHs. The five most commonly

used diagnostic ratios were used to infer the sources of PAHs in the sediment samples: Ant/(Ant + Phe), Fla/(Fla + Pyr), Fla/Pyr, BaA/(BaA + Chry), and BaA/BghiP. The sources of PAHs represented by the threshold values of each diagnostic ratio have been reported in several studies (Zhao et al., 2021; Abd Manan et al., 2021; Rostami et al., 2019; Li et al., 2021; Kurwadkar et al., 2022; Ambade et al., 2022). Ant/(Ant + Phe)  $< 0.1$  indicates petrogenic sources, Ant/(Ant + Phe)  $> 0.1$  indicates pyrogenic sources; Fla/(Fla + Pyr)  $< 0.4$  indicates petrogenic sources,  $0.4 < Fla/(Fla + Pyr) < 0.5$  indicates fossil combustion, Fla/(Fla + Pyr)  $> 0.5$  indicates grass, wood and coal combustion; Fla/Pyr  $< 1$  indicates petrogenic source, Fla/Pyr  $> 1$  indicates combustion sources; BaA/(BaA + Chry)  $< 0.2$  indicates petrogenic sources, BaA/(BaA + Chry)  $> 0.35$  indicates pyrogenic sources, and  $0.2 < BaA/(BaA + Chry) < 0.35$  suggests a mixture of PAH sources.

## 2.7. Ecological risk assessment

### 2.7.1. Hazard index (HI)

The Hazard Index (HI) was used to assess potential ecological risks for monitoring purposes (Abd Manan et al., 2021; USEPA, 1994). The Hazard Quotient (HQ) is based on the concentration of pollutants divided by their toxicity value (Eq. (1)). The cumulative HQ for all individual hydrocarbons (i.e., isomers detected) determines the Hazard Index (HI) for total hydrocarbons (Eq. (2)).

$$HQ_{\text{Ecological}} = \frac{C_i}{TRV} \quad (1)$$

$$HI = \sum_{n=1}^{\infty} HQ \quad (2)$$

where  $C_i$  is the concentration of an individual hydrocarbon (e.g., isomers),  $TRV$  is the toxicity reference value. The chronic value for PAH adapted from Neff et al. (2005) was used as the  $TRV$  for PAHs (Supplementary Table 1).  $TRV$  for TPH was obtained from Massachusetts Department of Environmental Protection and the values used were  $3.17 \text{ ng g}^{-1}$  for C10–C18 and  $9.88 \text{ ng g}^{-1}$  for C20–C32 (MassDEP, 2007). A HI  $> 1$  represents high risk;  $0.1 < HI < 1$  represents medium risk, and  $HI < 0.1$  represents low risk (Neff et al., 2005).

### 2.7.2. Mean effects range-median quotient (MERMQ)

The mean effects range-median quotient (MERMQ) was used as a comprehensive ecological risk analysis which, as proposed by Long and MacDonald (1998). It was used to quantitatively predict the toxicity of various pollutants in estuary and marine sediments following Eq. (3):

$$MERMQ = \frac{\Sigma(C_i/ERM_i)}{n} \quad (3)$$

where  $C_i$  is the concentration of the contaminant  $i$ ,  $ERM_i$  is the Effects Range-Median (ERM) value of the contaminant  $i$  and  $n$  is the number of contaminants. The ERM data of the PAH congeners are shown in Supplementary Table 2. An MERMQ value  $< 0.1$  means the ecological risk is relatively low;  $0.11 > MERMQ < 0.5$  means the ecological risk is medium to low;  $0.51 > MERMQ < 1.5$  means the ecological risk is medium to high; and MERMQ value  $> 1.5$  means the ecological risk is high (Zhang et al., 2019; Huang et al., 2012).

### 2.7.3. Mean probable effects level quotient (MPELQ)

The mean probable effects level quotient (MPELQ) was used to determine the combined ecological effects of contaminants as was calculated as shown in Eq. (4) (Long and MacDonald, 1998; Li et al., 2021):

$$MPELQ = \frac{\Sigma(C_i/PELi)}{n} \quad (4)$$



**Table 1**

Different mean concentrations calculated from the surface coastal marine sediments (ng g<sup>-1</sup>, dry weight sediment) at 22 sampling sites along the west coast of Qatar.

Location	Sites	ΣAHs ng g <sup>-1</sup>	Σ PAHs, ng g <sup>-1</sup>	pH	Temp., °C	TOC, %	Sand, %	Silt, %	Clay, %	Sediment type
Dukhan	SD1	112.2	16.4	6.84	36.6	1.37	75.4	24.1	0.53	Silty Sand
	SD2	246.0	10.3	7.71	34.9	1.51	75.8	23.5	0.01	Silty Sand
	SD3	<LOD	2.72	7.92	35.4	0.92	98.06	1.89	0	Sandy
	SD4	6.59	0.19	7.61	34.6	0.8	100	0	0	Sandy
	SD5	62.0	0.12	7.67	34.4	0.79	100	0	0	Sandy
	SD6	53.6	<LOD	7.84	33.9	0.77	100	0	0	Sandy
	SD7	96.5	2.41	7.9	35.2	0.79	100	0	0	Sandy
	SD8	17.4	1.70	7.67	35.8	0.57	100	0	0	Sandy
	SD9	43.0	2.96	7.81	36.7	0.95	93.9	6.11	0	Sandy
	SD10	63.2	44.4	7.65	36.0	1.05	90.3	9.67	0	Sandy
	SD11	<LOD	2.57	7.41	40.9	0.92	99.2	0.80	0	Sandy
	SD12	<LOD	1.04	7.84	35.1	1.49	98.2	1.78	0	Sandy
	SD13	16.7	0.17	7.78	35.1	0.50	100	0	0	Sandy
	SD14	11.8	0.41	7.46	35.5	0.70	99.9	0.35	0	Sandy
	SD15	<LOD	3.72	7.42	35.2	0.83	96.1	3.84	0	Sandy
	SD16	<LOD	1.77	7.89	34.4	0.87	100	0	0	Sandy
	SD17	<LOD	16.3	8.07	34.7	1.00	90.7	9.30	0	Sandy
	SD18	<LOD	0.29	7.38	34.9	0.33	100	0	0	Sandy
	SD19	<LOD	5.46	8.05	34.4	1.01	100	0	0	Sandy
	SD20	111.4	0.59	7.95	33.6	0.72	99.7	0.30	0	Sandy
Zekreet <sup>a</sup>	SZK	<LOD	1.62	7.84	35.3	1.01	100	0	0	Sandy
Umm-Bab <sup>a</sup>	SUB	6.21	1.69	7.65	38.4	1.05	100	0	0	Sandy

Limit of Detection (LOD) for AHs was 0.1 ng g<sup>-1</sup> and for PAHs was 0.1 ng g<sup>-1</sup>.

<sup>a</sup>Reference sites: Zekreet (north) and Umm Bab (south).

where  $C_i$  is the concentration of an individual compound,  $n$  is the number of contaminants, and  $PEL_i$  is the probable effects level of the individual compound (CCME, 1999). The PEL data of the PAH congeners are shown in Supplementary Table 2.  $MPELQ \leq 0.1$  indicates a low potential risk,  $0.1 < MPELQ < 1$  indicates a moderate risk, and  $MPELQ > 1$  indicates a high risk (Long and MacDonald, 1998; Li et al., 2021).

#### 2.7.4. Toxic risk index (TRI)

The toxic risk index (TRI) was used to evaluate the pollutants' probable toxic effects level against the threshold effects level in sediments (Elezz et al., 2022). Eqs. (5) and (6) were used to evaluate the TRI of the sediment.

$$TRI_i = \sqrt{\frac{(C_i/TEL)^2 + (C_i/PEL)^2}{2}} \quad (5)$$

$$TRI = \sum_{i=1}^n TRI_i \quad (6)$$

where  $TRI_i$  is the toxic risk index of contaminant  $i$ ,  $C_i$  is the concentration of contaminant  $i$ ,  $TEL$  is the Threshold Effects Level and  $PEL$  is the Probable Effects Level of the contaminant. The  $TEL$  and  $PEL$  of the PAH compounds are shown in Supplementary Table 2. TRI pollution level is characterized as: no toxic risk ( $TRI < 5$ ), low toxic risk ( $5 < TRI < 10$ ), moderate toxic risk ( $10 < TRI < 15$ ), considerable toxic risk ( $15 < TRI < 20$ ), and very high toxic risk ( $TRI > 20$ ) (Elezz et al., 2022).

### 3. Results and discussion

#### 3.1. Sediment characteristics

The pH, temperature, TOC, and sediment type of the 22 sediment samples analyzed are shown in Table 1. The pH ranged from 6.84 to 8.07 with an average pH of  $7.7 \pm 0.3$  and the temperature ranged from  $33.6^\circ\text{C}$  to  $40.9^\circ\text{C}$  with an average value of  $35.5 \pm 1.6^\circ\text{C}$ . The TOC concentration ranged from 0.33% to 1.51% with an average of  $0.90 \pm 0.28\%$ , which was found to be lower than the previously reported value of 2.34% in the Dukhan area as reported by De Mora et al. (2010). The sediment sample type was mainly classified as sand in most sites except at sites

1 and 2, which contained 24.05% and 23.53% silt, respectively (Table 1). The coastal sediment of Qatar contains low percentage of silt and clay mainly due to sorting by the tidal currents that wash the lighter sediment particles away and leave the coarser fractions behind (Soliman et al., 2019).

#### 3.2. Concentration of AHs and PAHs

The concentrations of AHs were found to be significantly different ( $p < 0.05$ ) between the sampling sites, while no significant differences ( $p > 0.05$ ) were observed in the concentrations of PAHs. The AH concentrations of sediment samples ranged from  $<0.1$  to  $246 \text{ ng g}^{-1}$  while the PAH concentrations ranged from  $<0.1$  to  $44 \text{ ng g}^{-1}$ . The average AH concentration in sediments sampled at site SD2 ( $246 \pm 80 \text{ ng g}^{-1}$ ) was higher than any of the other sampling sites (Fig. 2). It is also evident that the sites in Group A (Dukhan) had significantly higher concentrations of AH than the reference sites SZK (Group B) and SUB (Group C) ( $p < 0.05$ ). The sediments from sites SD1 and SD2 contained higher silt and clay percentages than the other sites, which may have influenced the levels of AH in those sites (Table 1). The greater surface area of the silty sediment particles means there is a greater potential for adsorption of organic pollutants (Gautam et al., 2020; Zhang et al., 2019; Ambade et al., 2022).

The  $\Sigma 16$  PAHs were also observed high in sites with high percentage of silt and TOC concentration (Table 1, Fig. 3). TOC content is an important index for evaluating persistent organic pollutants (e.g., PAHs) in sediments because organic carbon directly affects the adsorption and migration of PAH in sediments (Zhang et al., 2019). Among the sampling sites, SD1 and SD2 obtained the highest silt percentage of 24.0% and 24.5% respectively which were also characterized with high  $\Sigma$ PAHs concentration. Sites SD1 and SD2 are located downstream near an enclosed coastal area where transportation by water circulation and deposition of pollutants may have influenced the levels (Bergknut et al., 2010). The highest  $\Sigma$ PAHs concentration of  $44.4 \text{ ng g}^{-1}$  was observed in site SD10 which may have been attributed to the proximity of residential and petroleum fields in addition to the 9.6% of silt content. The variation of PAH concentration in the sediments of western coast of Qatar may be explained by the differential re-suspension and re-deposition of sedimentary PAHs,

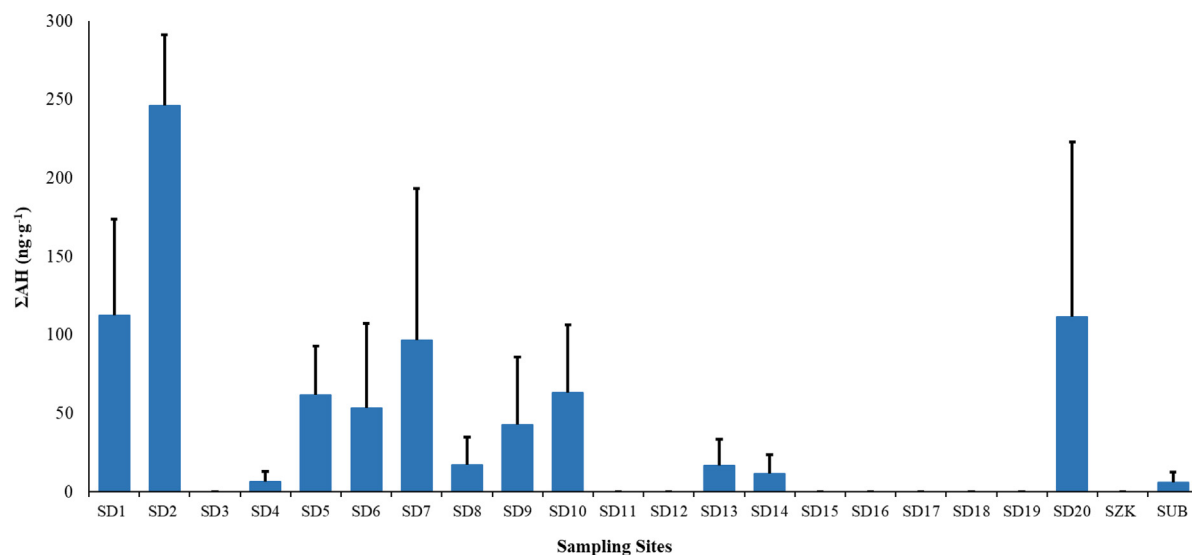


Fig. 2. Aliphatic hydrocarbon concentrations in coastal marine sediment samples collected along the western coast of Qatar.

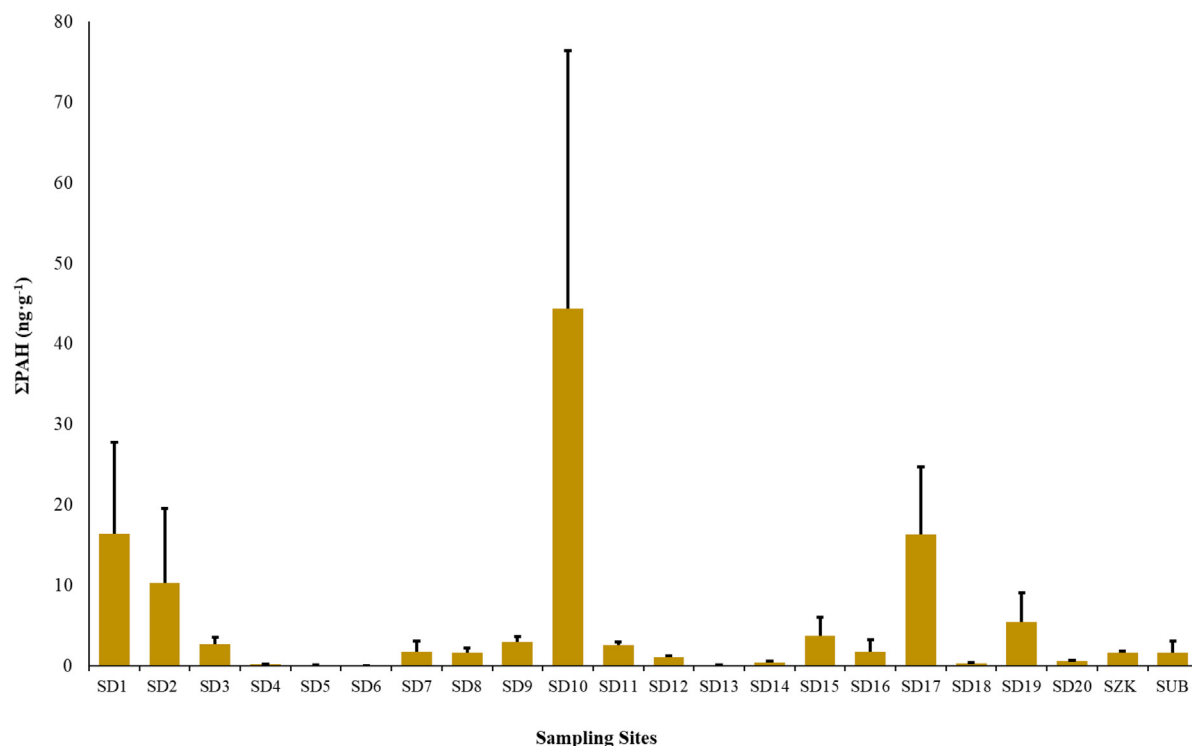


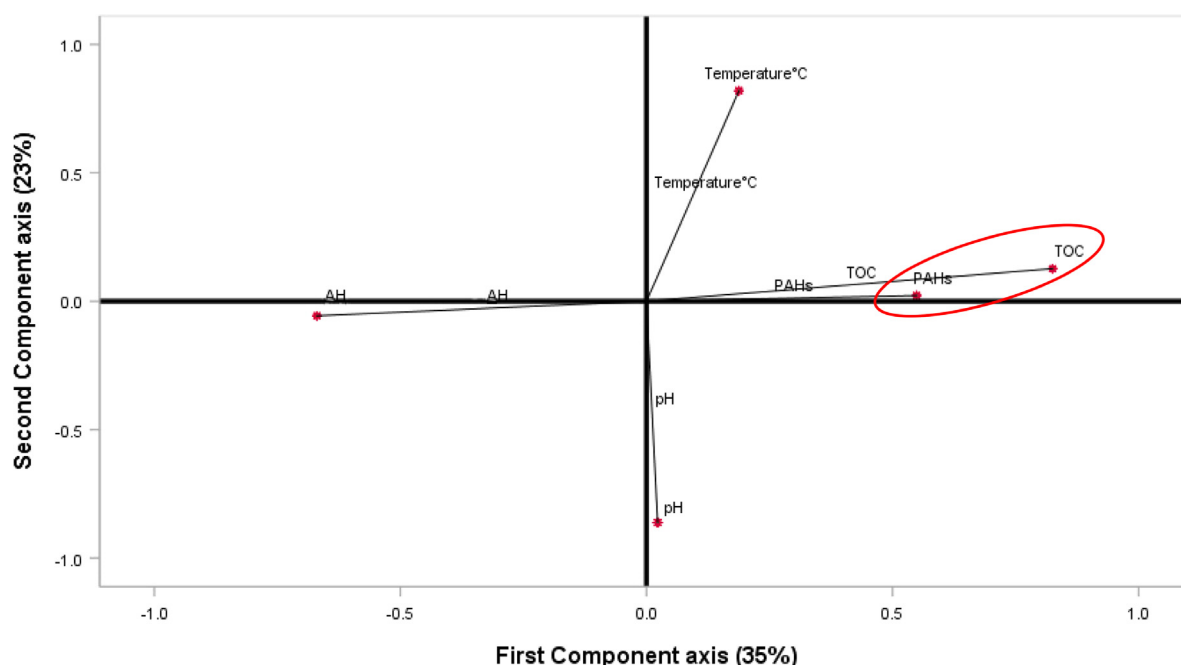
Fig. 3. Polyaromatic hydrocarbons concentrations in coastal marine sediment samples collected along the western coast of Qatar.

microbial degradation of PAHs, textural sedimentary composition, and vertical mixing due to physical or biological processes along with proximity to pollutant sources (Ambade et al., 2022).

Among the individual PAHs analyzed in the sediment samples, the concentrations of HMW PAHs were observed higher compared with the LMW PAHs (Supplementary Table 3). PAH with 4–5 rings were more dominant and had relatively higher concentrations. The 4 ring PAH compound Flu obtained the highest concentration of  $11.02 \text{ ng g}^{-1}$  observed in site SD10, followed by Pyr with concentration of  $9.2 \text{ ng g}^{-1}$  in the same station. The low solubility and hydrophobic nature of HMW PAHs facilitate their partitioning from aqueous to a solid phase (Kurwadkar et al.,

2022). A direct relationship is shown in the partitioning behavior of PAH between sediment and water phase with the number of PAH rings (Kurwadkar et al., 2022). The increased hydrophobicity of HMW PAH (higher number of rings) resulted to higher partitioning coefficients which explained the higher concentrations observed in HMW PAHs obtained in the study. The concentrations of 4–5 PAH member rings in sites SD1, SD2, SD10, SD17, SD19 were observed higher compared to the lower PAH member rings (Supplementary Table 3, Figure 3). The compositional analysis further showed that of the mean concentrations of the  $\Sigma 16$  PAHs were primarily composed of 2-ring (6%), 3-ring (18%), 4-ring (48%), and 5-ring (28%), 6-ring (0.14%) respectively.





**Fig. 4.** Principal Component Analysis (PCA) showing the correlation between the petroleum hydrocarbons pollutants and the physical parameters in the sediment samples.

**Table 2**  
Correlation matrix of sediment variables (n = 66).

	PAHs	TOC	AH	pH	Temperature (°C)
PAHs	1				
TOC	.276 <sup>a</sup>	1			
AHs	−0.038	−.340 <sup>b</sup>	1		
pH	−0.093	−0.084	0.056	1	
Temperature	0.263 <sup>a</sup>	0.239 <sup>a</sup>	−0.154	−.430 <sup>b</sup>	1

<sup>a</sup>Correlation is significant at the 0.05 level (2-tailed).

<sup>b</sup>Correlation is significant at the 0.01 level (2-tailed).

### 3.3. Correlations between sediment petroleum hydrocarbon concentrations and physicochemical parameters

Pearson's Correlation Coefficient was used to examine relationships between the studied variables in sediment samples (Table 2) and PCA was performed in order to plot using the correlation matrix of the relationships between AH, PAH and the physical parameters (i.e., pH, temperature and TOC). The eigenvectors that resulted from the PCA were plotted in the plane of the first two principal components: the first (PC1 = 35%) and second (PC2 = 23%) principal components explained 58% of the total variance in the dataset (Fig. 4). Vectors (parameters) pointing and clustering in the same direction indicate that they are highly positively correlated. There was a significant positive correlation between PAH and TOC ( $r = 0.276$ ;  $p < 0.05$ ). Previous studies have also demonstrated a positive correlation between PAH, TOC, and sediment grain size (Huang et al., 2012; Soliman et al., 2019). The PAH concentrations in the marine sediments that we sampled from the western coastline of Qatar were higher in the sediments with higher TOC and silt content (Table 1). TOC enhances sorption of hydrocarbons to sediment particles (Huang et al., 2012) and the finer grain size of the silty sediments has greater surface area to volume ratio than sand particles, therefore results in a greater adsorption capacity for hydrophobic PAHs (Wang et al., 2015b). The data obtained from this study indicated that only sampling sites which have silty sediments have relatively high TOC, in conjunction with high PAH concentrations.

The Pearson correlation analysis showed TOC had a significant positive correlation with PAHs ( $r = 0.276$ ;  $p < 0.05$ ), but a significant inverse correlation with AH ( $r = -0.340$ ;  $p < 0.01$ ). AH concentrations, on the other hand, did not significantly correlate with PAH concentrations ( $p > 0.05$ ). These findings agree with de Mora et al. 2010, who concluded that TOC cannot be used as an indicator for total petroleum hydrocarbon pollution. The average TOC content in the marine sediment of Qatar is generally low ( $0.90 \pm 0.28\%$ ). The country's coastal sediments are rich in carbonates (inorganic carbon) and mainly consist of dolomite, magnesium calcite and aragonite (Rivers et al., 2019). Wang et al. (2008) observed in their study that the components of carbonates determined the superficial state of sediments and their presence, together with organic matter, affects the sorption and desorption of petroleum hydrocarbon pollutants; particularly those with low molecular weight. In our study, carbonate rich (with low TOC content) and particularly low surface area of sandy sediments (considering the majority of the sediments samples in this study consist of 75%–100% sand) might have hindered adsorption desorption of petroleum hydrocarbon concentration, especially in the arid climatic conditions of Qatar. Tidal fluctuations may have also influenced the concentrations especially during low tide where the area is exposed to arid sun and possibly loss hydrocarbon concentrations due to intense evaporation (Hassan et al., 2018; Soliman et al., 2014; Rostami et al., 2019). Moreover, the degradation rate and degradation products of these pollutants are controlled by environmental conditions such as pH, temperature, and redox conditions (Rostami et al., 2019). In our study, temperature was found to have had a significant positive correlation with TOC content ( $r = 0.239$ ;  $p < 0.05$ ) and PAH concentrations ( $r = 0.263$ ;  $p < 0.05$ ). Similar results were observed by (Soliman et al., 2019). Temperature is an important factor in the seasonal variation of PAHs concentrations (Zhao et al., 2017). High temperature decreases the viscosity of hydrocarbons and consequently affects their degradation and decreases their lifetime (Mu et al., 2018). pH, on the other hand, did not correlate with PAH concentration, AH concentration, or TOC content. However, pH was inversely correlated with temperature ( $r = -0.430$ ;  $p < 0.01$ ). It is unlikely that it directly contributed to the weathering or level of the petroleum hydrocarbon contaminants in the sediments.

**Table 3**

Aliphatic (AH) and polyaromatic hydrocarbon (PAH) concentrations in surface marine sediments ( $\text{ng g}^{-1}$ , dry weight sediment) from different Gulf regions over the last two decades.

Year	Region	AH, $\text{ng g}^{-1}$	PAHs, $\text{ng g}^{-1}$	Reference
1991	UAE	260–460	4000–6100	Fowler et al. (1993)
	Saudi Arabia	900–23 000	5700–175 000	
	Bahrain	260–2600	3300–7900	
	Oman	100–1200	1900–5700	
1993	Gulf	1500–79 300	–	Al-Omran and Rao (1999)
2000	Qatar	70–3300	0.55–92	Tolosa et al. (2005)
	UAE	38–1100	0.39–9.4	
	Bahrain	670–4300	13–1000	
	Oman	11–240	1.6–30	
2005	Qatar	100–4400	9–136	De Mora et al. (2010)
	Saudi Arabia	400–2300	12–125	
	UAE	200–1600	6–139	
	Kuwait	200–2700	12–1670	
	Oman	100–1400	0.3–543	
	Iran	300–1100	37.6–497	
	Bahrain	700–4400	13.6–3540	
2014	Qatar, east	–	3–1030	Soliman et al. (2014)
2016	Qatar, east	–	3.15–14.35	Hassan et al. (2018)
2018	Qatar, west	–	1–1560	Soliman et al. (2019)
2019	Present study, Qatar, west <sup>a</sup>	<LOD–246	<LOD–44	

<sup>a</sup>Limit of detection (LOD) for AH was  $0.1 \text{ ng g}^{-1}$  and for PAHs was  $0.1 \text{ ng g}^{-1}$ .

### 3.4. Comparisons with other studies

AH and PAH concentrations reported in the present study were compared with several published studies of marine sediments from different Gulf regions in the Middle East (Table 2). The concentrations of AHs and PAHs in the sediments of the western coast of Qatar fall within the range of the results from other locations listed but are relatively low in comparison with other Gulf coasts. The reported concentrations of AHs and PAHs in the study of Tolosa et al. (2005) were in the range of 70–3300 and  $0.55\text{--}92 \text{ ng g}^{-1}$ , respectively, which were generally higher than the concentrations reported in this study (Table 3). The concentrations of sediment organic hydrocarbons in the Gulf were generally high before and immediately after the 1991 Gulf war, reaching up to  $79\,300 \text{ ng g}^{-1}$  for AH (Al-Omran and Rao, 1999) and  $175\,000 \text{ ng g}^{-1}$  for PAH off the coast of Saudi Arabia (Fowler et al., 1993), but have since declined considerably in the past 3 decades. The recent study by Soliman et al. (2019), undertaken in a similar area (west coast) to our study, reported higher PAH concentrations than our results. However, their concentrations were still much lower than those observed 3 decades ago. The PAH concentrations in the sediments of the east coast of Qatar, reported in the study by (Hassan et al., 2018) were lower than the concentrations in our study. A decrease in the concentrations of AHs and PAHs may have been due to weathering, evaporation, and solubility of low molecular weight hydrocarbons, which is affected by temporal and spatial variability (Cui et al., 2016; Soliman et al., 2019; Ambade et al., 2022). Based on the concentration ranges, the pollution level of PAHs is categorized as low pollution ( $<100 \text{ ng g}^{-1}$ ), moderate pollution ( $5000 \text{ ng g}^{-1}$ ), and very high pollution ( $>5000 \text{ ng g}^{-1}$ ) (Ambade et al., 2022). Based on these criteria, all our sampling sites were deemed to have low pollution. A pollution concentration profile is site specific depending on proximity to the source and on the transport, re-distribution, and re-suspension of contaminants which, in turn, are affected by coastal hydrodynamic processes, such as tidal currents (Yang et al., 2018; Soliman et al., 2019). The arid climate in Qatar, which includes extreme high temperature conditions, especially in the summer, enhances the loss of hydrocarbons by affecting the contaminant's partitioning coefficient between organic and aquatic

phases (Cui et al., 2016; Kurwadkar et al., 2022). These processes are implicated by the very low concentration ( $<0.1 \text{ ng g}^{-1}$ ) for NaP and Acl PAH compounds observed in sediment sampled at most of our sites, implying dissolution and/or evaporation of low MW PAHs (Supplementary Table 3). Enforcement of regulations and the use of more advanced environmental protection technologies in different phases of oil and gas extraction, production, and transportation may be responsible for the decline in the petroleum pollution concentrations observed here, compared to previous surveys (Soliman et al., 2019).

### 3.5. Identification of AHs sources

#### 3.5.1. The LMW/ HMW AH index

Natural samples consist of complex hydrocarbon mixtures and several parameters were used as distinct diagnostic ratios to identify possible sources of petroleum hydrocarbons in sediments. Concentrations of LMW or HMW below the detection limits (LOD =  $0.1 \text{ ng g}^{-1}$ ) resulted in the inability to calculate the LMW/ HMW index for nine out of twenty-two studied sites (Table 1). The low levels could be attributed to the weathering of the aliphatic (*n*-alkanes) components of the petroleum hydrocarbons. Some petroleum oil residues from the north-western side of the Qatar in another study were found to be highly weathered and likely originated from an old oil spill during the 1991 Gulf War (Arekhi et al., 2020). However, sites SD1 to SD10 (except SD3) had a higher level of LMW than HMW AH, which indicates a fresh input of oil residues. These sites are located towards the south end of the onshore oil and gas field. Hydrodynamic processes (e.g., tidal currents and wind patterns) could possibly have directed and concentrated oil residues at these sites (Rivers et al., 2019). Sites SD13 and SD14 had a lower level of LMW than HMW, which is indicative of a terrigenous plant source. In this study, the diagnostic ratio between LMW/HMW AH demonstrated the origin of the aliphatic hydrocarbons as derived from both petroleum products and plant biomass (Rostami et al., 2019; Seopela et al., 2020). Similar observations were reported in the studies of (Venturini et al., 2008; Rostami et al., 2019; Seopela et al., 2020).

### 3.5.2. The $\Sigma n$ -Alkanes/ $n$ -C16 index

The comparative abundance of  $n$ -alkanes with different carbon numbers ( $n$ -C10 to  $n$ -C32) in the sediment also suggests the source of the hydrocarbons in the sediment samples. The  $\Sigma n$ -Alkanes/ $n$ -C16 ratio was less than 50 for all the samples. The ratio ranged from 0.00 to 35.19 in the sediments. A relatively low  $\Sigma n$ -Alkanes/ $n$ -C16 ratio indicates the presence of hydrocarbons of fossil origin (Rostami et al., 2019). The abundance of the low molecular weight even carbon numbered alkanes ( $n$ -C10–18) in the study over the higher molecular weight ( $n$ -C20–34) alkanes suggests a petrogenic origin of hydrocarbons. Other sites however had concentrations below the detection limit which suggests absence of aliphatic hydrocarbons.

## 3.6. Identification of PAHs sources

### 3.6.1. The LMW/HMW PAH index

Spatial variations were observed in the weight ratio of LMW/HMW PAHs which ranged from 0.00 to 3.16. PAH sources in the study were derived from both direct inputs of petroleum and combustion sources. Sites SD9, SD11, and SD14 had a LMW/HMW PAH ratio of 1.97, 2.16 and 1.60, respectively, which suggests petrogenic sources. Sites SD1, SD2, SD3, SD10, SD15, SD16, SD17, SD19, SUB, and SZK had LMW/HMW PAH ratios < 1 which indicates pyrolytic sources. Sites SD4, SD5, SD6, SD13, and SD18 had undetermined LMW/HMW PAH ratios since the concentration of the individual PAH isomers in these sites were less than the method detection limit (LOD = 0.1 ng g<sup>-1</sup>).

Petrogenic PAH sources enter the marine environment from leakage and transport of crude oil or refined substances (e.g., gasoline and diesel fuel from ships, and wastewater effluents), while pyrolytic PAH comes from the combustion of these products during refining processes (i.e., flare stacks) (Rostami et al., 2019), carbonization of coal and oil to produce manufactured gas, coal tars, and catalytic cracking of petroleum feed stocks (Neff et al., 2005). High temperature combustion processes produce high molecular weight PAH compounds and the predominance of these HMW PAHs may be related to the deposition, slow degradation, and persistence of these compounds in marine sediments (Kurwadkar et al., 2022). The sediment samples in the present study were enriched with 4–5 ring PAHs including acenaphthene, phenanthrene, and anthracene, which are characteristic of pyrogenic sources (Supplementary Table 3, Neff et al., 2005). In the Gulf region, precipitation is scarce. Therefore, dry deposition or air–water gas exchange between atmospheric PAHs (i.e., vapor phase) and surface waters are probably the main source of pyrogenic PAHs (Soliman et al., 2019).

### 3.6.2. PAH isomer diagnostic ratios

Isomeric ratios were used to differentiate the sources of PAHs at our study sites with respect to petroleum or combustion sources. The Ant/(Ant + Phe) ratio ranged from 0 to 0.66. Fifteen out of 22 sites indicated PAHs of pyrolytic origin, while 7 sites had an Ant/(Ant + Phe) ratio of 0 (Fig. 5a). The Fla/(Fla + Pyr) ratio ranged from 0.00 to 0.63. Two sites were indicated to contain PAHs of petrogenic source, 1 site indicated fossil combustion, 4 sites indicated biomass and coal combustion while 15 sites reported a Fla/(Fla + Pyr) ratio of 0 (Fig. 5a). The BaA/(BaA + Chry) ratio ranged from 0.00 to 0.68. The ratio at five sites suggested a pyrogenic source, 5 sites suggested mix PAH sources, while 11 sites had a BaA/(BaA + Chry) ratio of 0 (Fig. 5b). The Fla/Pyr ratio ranged from 0.00 to 1.71. The ratio at three sites indicated a petrogenic source, 4 sites indicated a pyrolytic source while the ratio at 15 sites was 0 (Fig. 5c).

Boonyatumanond et al. (2006) considered BghiP as an indicator of a traffic-derived PAHs. Larsen and Baker (2003) also

concluded that 6-ringed PAHs (InP, DahA, and BghiP) were mainly derived from diesel combustion and exhaust emissions from automobile engines. Among the PAH isomers analyzed, InP, DahA, and BghiP showed concentrations below the limit of detection (LOD = 0.1 ng g<sup>-1</sup>) in all sampling sites (Supplementary Table 3). Therefore, the study suggested a mixture of PAH sources, but no evidence of vehicular traffic as a source. The sampling sites in this study were indeed away from concrete roads and automobile traffic.

## 3.7. Calculation of ecological risk

### 3.7.1. Hazard index (HI)

HI is an ecological risk assessment used to estimate the health hazard of pollutants based on their chronic toxicity values. The HI for PAHs in the study ranged from 0.00 to 9.42. Approximately 32% of the sampling sites from the western coast of Qatar had HI value indicating high risk, 23% medium risk and 45% low risk in terms of PAH compounds. The high HI values in the study were mostly due to 4 and 5 ring PAHs (fluoranthene to benzo(a)pyrene) which are predominantly of pyrogenic origin. Other predominantly pyrogenic PAHs, which also contributed to the HI, include acenaphthene and anthracene (Supplementary Table 3). High molecular weight pyrogenic PAHs (e.g., in soot or coal tar, and related viscous liquids) are often bound to sediment particles more strongly than predicted by the equilibrium partitioning theory (Neff et al., 2005; Kurwadkar et al., 2022). Mitra et al. (1999) showed that the high molecular weight PAHs have a much higher log K<sub>oc</sub>, indicating a low accessibility and low bioavailability. It is therefore likely that the sediments are much less toxic to benthic organisms than predicted by the high HI values.

For aliphatic hydrocarbons, the HI for C10–C18 ranged from 0.00 to 25.86 while the HI for C20–C32 AHs ranged from 0.00 to 16.60. The higher HI values in LMW C10–C18 may be attributed to petroleum associated sources, as evidenced by the higher LMW/HMW AH ratio. Petroleum hydrocarbons with lower molecular weights, such as gasoline, are highly volatile when accidentally inhaled or ingested and can lead to systematic organ and lung damage (e.g., pulmonary oedema and bronchopneumonia) (Gupta, 2016).

### 3.7.2. MERMQ and MPELQ

The potential ecological risk level of each PAH compounds in this study was evaluated according to the standard set by the NOAA and CSQG (Table 4). We used the approaches of Effects Range Low (ERL), Effects Range Medium (ERM), Threshold Effects Level (TEL) and Probable Effects Level (PEL). ERL and TEL are representative of lower concentrations that rarely lead to harmful biological effects while ERM and PEL are suggestive of higher levels that frequently have destructive biological effects (Yancheshmeh et al., 2014). The results indicate that the concentration of each PAH compound was much lower than the ERL and TEL, suggesting that PAH contamination in the sediments along the west coast of the country had low ecological risk level (Table 4).

Long and MacDonald (1998), also proposed the Mean ERM quotient (MERMQ) and Mean Probable effects Level (MPELQ) methods for quantitative prediction of the comprehensive ecological toxicity of PAHs. Using these methods, the calculated MERMQ value ranged from 0.00 to 0.0014 while the calculated MPELQ value ranged from 0.00 to 0.0042. Despite Qatar being exposed to petroleum industry activity, the PAHs concentrations were found to be of low ecological risk. These data are consistent with the comparisons of the threshold values reported in Table 4.

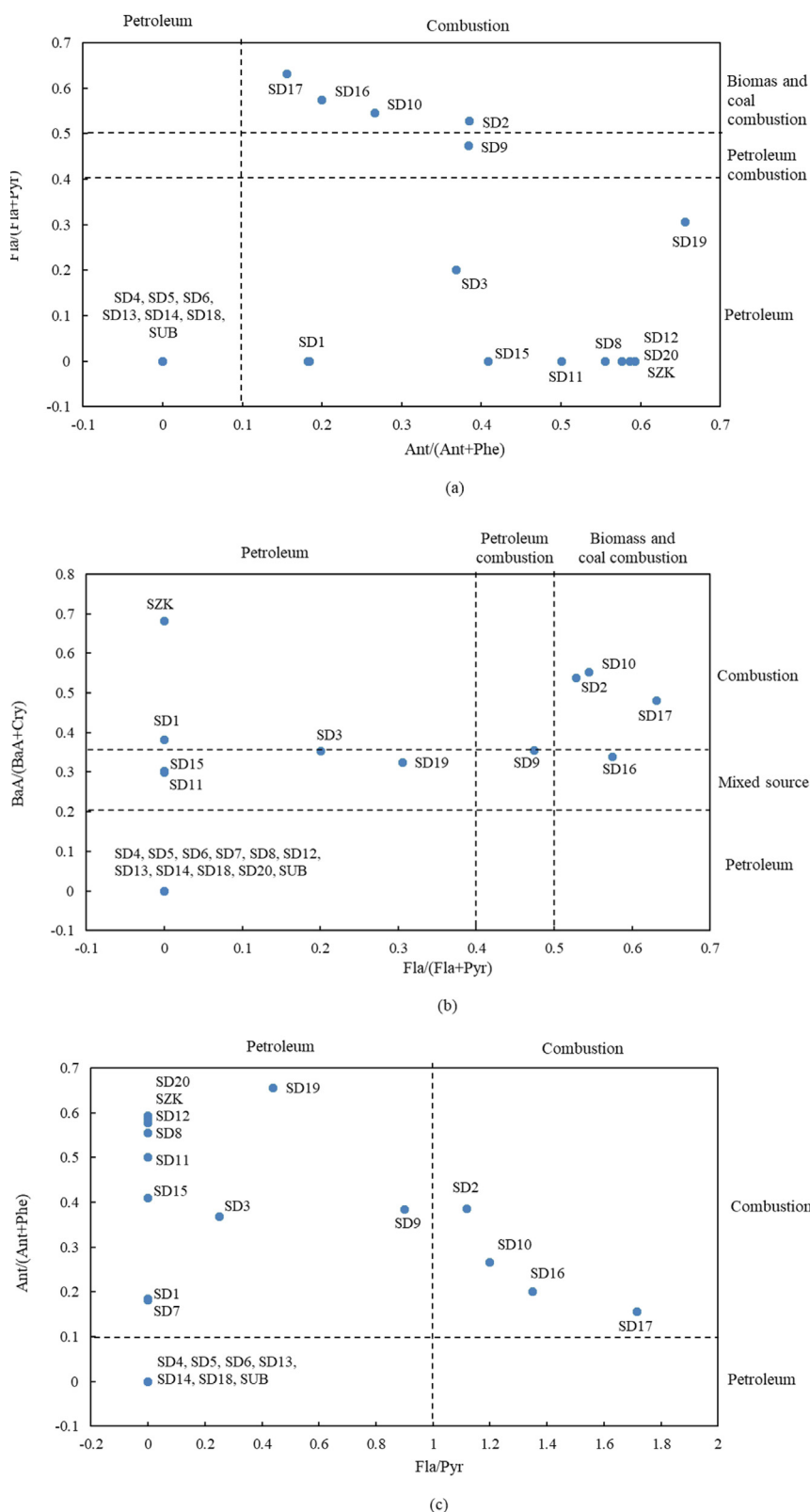


Fig. 5. Different diagnostic ratios (a, b, c) of PAH sources at different sampling sites.

### 3.7.3. The Toxic Risk Index (TRI)

Unlike MERMQ and MPELQ, the TRI considers both TEL and PEL effects which provides a more comprehensive risk assessment of pollutants to the environment (Elezz et al., 2022). The TRI of the

current study, calculated using Eq. (6), ranged from 0.00 to 0.32. The average TRI value in the entire west coast of Qatar was 0.04. Sites SD4, SD6, SD13, SD18 had a TRI value of 0, while site SD10 had the highest TRI value of 0.32. Based on the TRI values, our



**Table 4**

Comparison of the PAH concentration with the NOAA and CSQG guideline values.

Source: Buchman (2008), CCME (1999), Nascimento et al. (2017) and Long et al. (1995).

PAHs	NOAA ng g <sup>-1</sup>		Individual PAH Range (ng g <sup>-1</sup> )	CSQGs ng g <sup>-1</sup>	
	ERL	ERM		TEL	PEL
Naphthalene	160	2100	<LOD-1.35	34.6	391
Acenaphthylene	44	640	<LOD	5.87	128
Acenaphthene	16	500	<LOD-0.42	6.71	88.9
Fluorene	19	540	<LOD-0.32	21.2	144
Phenanthrene	240	1500	<LOD-5.14	86.7	544
Anthracene	85.3	1100	<LOD-1.87	46.9	245
Total LMW PAHs	552.0	3160	<LOD-8.58	312	1442
Fluoranthene	600	5100	<LOD-11.02	113	1494
Pyrene	665	2600	<LOD-9.20	153	1398
Benzo(a)anthracene	261	1600	<LOD-3.88	74.8	693
Chrysene	384	2800	<LOD-3.14	108	846
Benzo(b)fluoranthene	–	–	<LOD-4.17	–	–
Benzo(k)fluoranthene	–	–	<LOD-3.22	–	–
Benzo(a)pyrene	430	1600	<LOD-1.86	88.8	763
Indeno(1,2,3-cd)pyrene	–	–	<LOD	–	–
Dibenz(a,h)anthracene	63.4	260	<LOD-0.16	6.22	135
Benzo(g,h,i)perylene	–	–	<LOD	–	–
Total HMW PAHs	1700	9600	<LOD-35.82	655	6676
Total PAHs	4022	44 792	<LOD-44.41	1684	16 770

National Oceanic and Atmospheric Administration (NOAA); Canadian Sediment Quality Guidelines (CSQG); Limit of Detection (LOD) < 0.1 ng g<sup>-1</sup>; Effects Range Low (ERL); Effects Range Medium (ERM); Threshold Effects Level (TEL); and Probable Effects Level (PEL).

results indicated low ecological risk, which agrees with the results of the other ecological risk assessment approaches described above.

The TEL for AHs stated in the Environment Protection Law, 2002 set by Ministry of Municipality and Environment of Qatar is equivalent to 5000 ng g<sup>-1</sup> (Qatar EPL, 2002). The concentrations of AHs in sediments we sampled along the west coast of the Qatar were well below this limit, also suggesting low ecological risks resulting from AH contamination.

#### 4. Conclusions

This study examined the distribution, source apportionment, and potential ecological risk of AHs and PAHs in the intertidal marine sediments along the western coast of Qatar. The study investigated whether the proximity of oil and gas extraction operations have contributed to the levels of petroleum hydrocarbon contaminants in the marine environment. The  $\Sigma$ AHs concentrations ranged from <0.1 to 246 ng g<sup>-1</sup> while the  $\Sigma$  PAHs concentrations ranged from <0.1 to 44 ng g<sup>-1</sup>. High  $\Sigma$ AHs were observed in sites SD1 (112.2 ng g<sup>-1</sup>), SD2 (246.0 ng g<sup>-1</sup>), SD7 (96.5 ng g<sup>-1</sup>), SD10 (63.2 ng g<sup>-1</sup>) and SD20 (111.4 ng g<sup>-1</sup>) while  $\Sigma$ PAHs on were observed high in SD1 16.4 ng g<sup>-1</sup>), SD2 (10.3 ng g<sup>-1</sup>), SD10 (44.4 ng g<sup>-1</sup>), SD 17 (16.3 ng g<sup>-1</sup>). There was a positive correlation between PAH and percentage silt and TOC content. The data indicated that only sampling sites which have silty sediments with high TOC content have high PAH concentrations. On the contrary, there was no correlation between TOC and AH concentration. Our findings agree with other studies that TOC is a good indicator of PAH but not for AH. The results obtained for AH and PAH were comparable and the concentration ranges were towards the lower end of concentration ranges reported in studies within Gulf regions. The variation of AH and PAH concentration in the sediments of western coast of Qatar may be explained by the differential re-suspension and re-deposition of the contaminants, solubility and microbial degradation of petroleum hydrocarbons, textural sedimentary composition, vertical mixing due to physical or biological processes and proximity to pollutant sources.

Diagnostic ratios and hydrocarbon parameters suggested mixed sources i.e., petrogenic, pyrolytic, biomass, but no evidence of vehicular traffic as a source was found. LMW/ HMW AH index for

nine out of twenty-two studied sites were < LOD indicative of absence of AH. The low level may be attributed to weathering of aliphatic (*n*-alkanes) components of the petroleum hydrocarbons. Sites SD1 to SD10 (except SD3) had a higher level of LMW than HMW AH indicative of fresh input of oil residues. Moreover, the abundance of the LMW even carbon numbered alkanes (*n*-C10–18) in the study over the HMW (*n*-C20–34) alkanes suggests a petrogenic origin of hydrocarbons. Source of PAH on the other hand is suggestive of petrogenic and pyrolytic origin. HMW PAH were predominant over LMW PAH. The compositional analysis mean concentrations of the  $\Sigma$ 16PAHs were composed of 2-ring (6%), 3-ring (18%), 4-ring (48%), 5-ring (28%), and 6-ring (0.14%), respectively. Among the PAH isomers analyzed, InP, DahA, and BghiP showed concentrations < LOD in all sampling sites. These isomers are indicator of traffic-derived PAHs therefore its absence means no vehicular traffic source. Petrogenic sources enter the marine environment from leakage and transport of crude oil or refined substances, while pyrolytic source comes from the combustion of these products during refining processes (i.e., flare stacks).

Overall, the results obtained from the present study can be concluded that the oil and gas production activities along the western coastline of Qatar did not have a direct impact on the marine sediments to the extent that environmental quality standards are violated. The results for AH and PAH were below the threshold limit set by NOAA and CSQG. Concentration profile were also found to have low pollution based on the pollution criteria. The data presented here represent a valuable quantification of petroleum hydrocarbons that would be essential to assess the impact associated with future onshore anthropogenic activities and identify remediation goals in the event of an environmental pollution incident. Continued long term-monitoring is also required to ensure that the levels of these organic pollutants do not exceed the current levels. Further studies would be beneficial to investigate the atmospheric deposition of these petroleum hydrocarbon contaminants and their levels in the marine waters and organisms, especially in this part of the country, to compare and evaluate their exposure to environmental pollution.

#### CRedit authorship contribution statement

**Maryam A. Abdulla:** Writing – original draft and editing, Conceptualization, Data curation, Methodology, Formal analysis.

**Azenith B. Castillo:** Writing – original draft and editing, Conceptualization, Data curation, Methodology, Writing – review & editing. **Christopher Collins:** Supervisor, Review & editing. **Tom Sizmur:** Co-Supervisor, 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

Data will be made available on request

### Acknowledgments

Thanks to Environmental Science Center (ESC), Qatar University and all ESC members, especially Prof. Abdelbary, Dr. Al-Khayat, Ms. Al-Naimi (Technical Manager), Ms. Ibrahim, Ms. Aljathelah, Ms. Ályafei and Mr. Ahmed (map). Thanks to Mr. Elobaid and Mr. Gasang for their assistance during fieldwork and to Ms. Ruqaiya Yousif from ExxonMobil, Qatar doing the GIS mapping. The authors acknowledge the Open Access funding provided by the Qatar National Library.

### Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.rsma.2023.103042>.

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