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Assessment of ecological risk and identification sources of polycyclic aromatic hydrocarbons at coastal sediments: A case study in Bushehr Province, Iran

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Abstract

Background: Polycyclic aromatic hydrocarbons (PAHs) are stable and highly toxic environmental pollutants, which are produced mainly through combustion processes. The present study aimed to identify and determine PAHs compounds and their ecotoxicological effects in surface sediments of 20 stations in Bushehr province (Assaluyeh, Kangan, Khark, Emam Hasan, and Bushehr areas).

Methods: All sediment samples (0-5 cm) were collected from 20 sites of Persian Gulf costs (Bushehr province, Iran). The concentration of PAHs was determined by HPLC. Then, in order to identify the sources of PAHs, ΣLPAHs/ΣHPAHs, IP/ (IP + BP), PH/AN, and AN/(PH + AN) ratios were obtained. Sediment quality guidelines (SQGs) and sediment quality criteria (SQC) were used to measure the PAHs ecotoxicological effects in sediments.

Results: Based on PAHs isomeric ratios, the contaminants of sediments originated from pyrogenic resources. ΣPAHs values (ng/g dw) in sediment samples ranged from ND to 49180. The toxic equivalent concentration (TEQ car) of PAHs raged from ND-7999 ngTEQ/g. Based on SQGs and SQC, the concentrations of ΣPAHs compounds in 10% and 6% of the sampling stations exceeded effects range median (ERM) and frequent effect level (FEL), respectively, indicating negative ecological risk effects.

Conclusion: Sampling stations sediments must be routinely checked for PAHs because may lead to a negative effect on the marine ecosystem, organisms, and humans.

Keywords: Polycyclic aromatic hydrocarbons, Ecosystem, Environmental pollutants, Chromatography, Ecotoxicology, Geologic sediments

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the main contaminants produced using defective ignition of organic compositions at pyrolysis (1-7). The PAHs generic structure is made of two and more aromatic rings in form of lineal, racemose, and angular (8). PAHs are mainly hydrophobic and organic lipophilic compounds, which are composed of hydrogen and carbon (9-11). PAHs composed of four or more aromatic rings are considered as heavy PAHs (HPAHs), whereas compounds with less than four rings comprise light PAHs (LPAHs) (12, 13). Exposure to PAHs causes adverse safety effects, including carcinogenic, reproductive defects, bioaccumulation, and mutagenic for humans and other organisms (14-17). PAHs can be formed in three ways: Pyrogenic, petrogenic, and biological (10,18-20). The persistent sources of PAHs in the environment are anthropogenic, such as ship transit, municipal runoff, petroleum leakage, water, and industrial sewage, which leads to the entry of PAHs into aquatic environments (2,21,22).

In aquatic environments, PAHs are placed on sedimentary material and may decrease their bioavailability and biodegradation, and then, be maintained in sediments for a lengthy period (23). Therefore, sediments are the basic tanks of PAHs in the aquatic environments, so that in suitable environmental conditions, precipitated PAHs can enter the water and lead to bioaccumulation in the food chain (24-26).

Bushehr province with a shoreline more than 707 km is located along the Persian Gulf in Iran southwestern. This province due to its strategic situation is one of the most momentous harbors in Iran and a major place for petroleum transportation. Because of the high compression of oil conveniences and significant increase of petroleum contamination risk, this region has become one of the damaged areas in the world. However, there is few information about PAH contaminations in all harbors of Bushehr province (27,28). The aim of this study was to present comparative and complete information about the PAHs pollution status in the sediments, feasible sources of PAHs and ecotoxicological effects of PAHs in 5 harbors (Asaluyeh, Kangan, Khark, Emam Hasan, and Bushehr) of Bushehr province.

Materials and Methods

Sampling

A total number of 300 sediment samples (15 samples from each station) (at depth of 0-5 cm) were collected from 20 sites of Persian Gulf costs (Bushehr province, Iran), by a clean stainless-steel spatula, in Assaluyeh, Kangan, Khark, Emam Hasan, and Bushehr coastal areas during January and February 2019 using GPS (Figure 1). The samples were placed into aluminum jar and stored on ice and transmitted immediately to the laboratory. In the laboratory, sediments were freeze-dried for 24 h, homogenized, transferred into a glass jar washed by n-hexane and covered in foil, and kept at -20°C until the test.

Analysis of PAHs

Standards of PAHs including benzo (g.h.i) perylene (BP), dibenz[a,h]anthracene (DA), pyrene (IP), benzo[a] pyrene (BaP), indeno (1,2,3,cd), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), Chrysene (CH), Pyrene (PY), fluoranthene (FLU), Anthracene (AN), phenanthrene (PH), fluorene (FL), acenaphthene (ACE), acenaphthylene (ACY), naphthalene (NA), benzo(a) anthracene (BaA), n-hexane, and dichloromethane, were purchased from Merck (Germany).

In order to analyze the PAHs, dried sediments (10 g) were mixed with 250 mL of n-hexane:dichloromethane at a volume ratio of 1:1, and the mixture was placed in Soxhlet for 8 hours. The combined extract was condensed on a rotary vacuum evaporator for 15 mL. Activated copper was added to remove sulfur and its compounds, then, the residual was passed through a filter paper

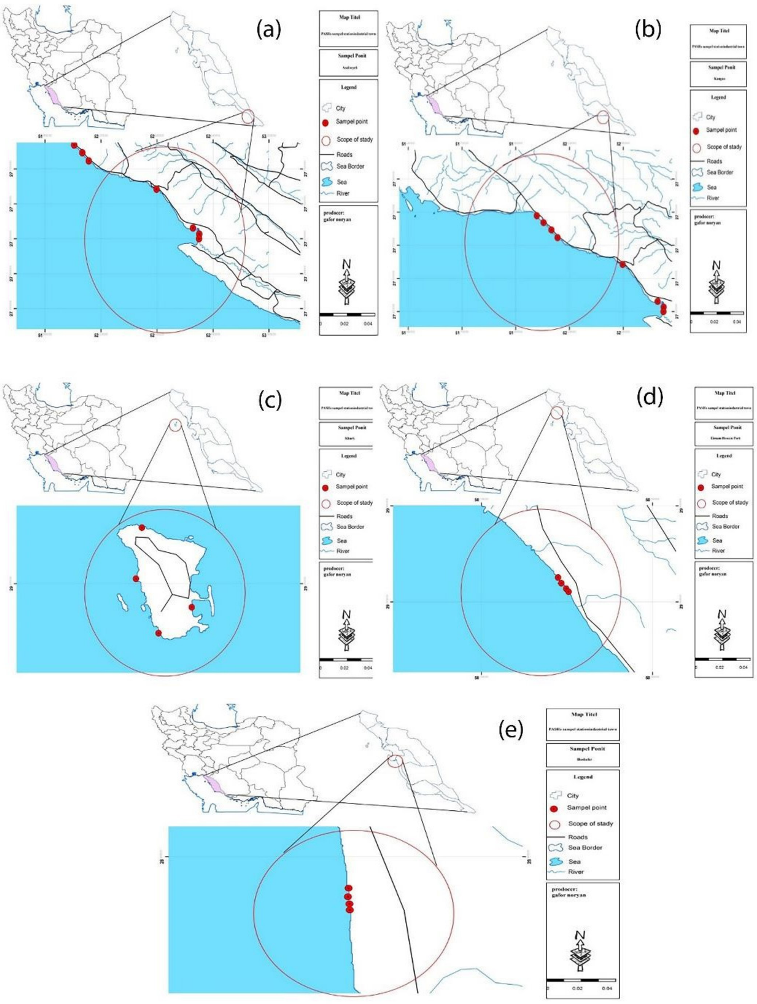

Figure 1. Plot of the study areas and sampling stations in the (a) Assaluyeh, (b) Kangan, (c) Khark, (d) Emam Hasan, and (e) Bushehr stations.

(Whatman GF/C, 24 microns) for 24 hours. The extract passed through a column including alumina (10 g), sodium anhydrous sulfate (2 g), and silica (10 g). The mixture of dichloromethane and n-hexane (30 mL) was added to the column at a volume ratio of 1:9. The content of the sample was regulated again at 5 mL. The extract was dried with a nitrogen gas stream, and then, 1 mL of acetonitrile was added to it (29).

The HPLC device (Younglin 9100) was employed to analyze the PAHs in the samples. HPLC was equipped with a fluorescence (Agilent 1100) and UV detector (youngling 9120). The column type of the reverse phase was C_{18} (250 × 4.5 mm, 5 µm). The initial mobile phase was HPLC grade water (60%) and acetonitrile (40%), which changed to 100% acetonitrile in 20 min and held at 100% for 7 minutes, then, reduced to the primary phase. Peak area of external standards (PAH mix, CRM47940, Supelco) and decachlorobiphenyl as internal standard (48318, Supelco) were used to obtain internal standard calibration curves and to measure the PAHs.

To obtain the recovery values of the method, a hexane-washed sediment was heated at 250°C for 12 hours and polluted with PAH mix solution at 500 ppb level. Then, the obtained sediment was treated as other samples. The recovery values ranged from 71% to 86% for all PAHs.

Source identification

The correlation ratios among the values of the single PAHs indicating that they all originated from one similar origin or not (30). Moreover, different sources of PAHs in sediments can be expected depending on PAHs composition. Low molecular weight (LMW, 2-3-ring) PAHs are produced by a petrogenic source, whereas high molecular weight (HMW, 4-6-ring) PAHs have a pyrogenic source. Therefore, ΣLPAHs/ΣHPAHs <1 shows pyrogenic sources and ΣLPAHs/ΣHPAHs >1 refers to petrogenic sources (31). In this study, PAH isomers including PH/AN and AN/(PH + AN) ratios were also used to evaluate possible sources of PAHs. PH/AN and AN/(PH + AN) ratios higher than 10 and lower than 0.1 indicate pollution of petroleum products, and ratios lower than 10 and higher than 0.1 show pyrogenic activities (3,22). The ratio of IP/(IP + BP) is also an important indicator of the PAHs sources assessment in sediments, which was also studied in this research. When the ratio of IP/(IP + BP) is lower than 0.2, it is originated from petrogenic sources and if it is between 0.2 and 0.5, demonstrates liquid fuel combustion, and a ratio more than 0.5 is related to combustion processes of solid fuel (32).

Ecological risk assessment

Sediment toxicity was calculated with the toxic equivalent factor (TEF). The toxicity evaluation of sediments was performed according to the values of total carcinogenic PAHs (cPAHs) including DA, BaP, IP, BkF, CH, BbF, and BaA. BaP (the most toxic combination of PAHs) was considered as the reference PAH, to which the TEF value of 1 was dedicated, whereas other combinations of PAHs had lower TEF values compared with the BaP. According to the United States Environmental Protection Agency (USEPA), the TEFs values for DA, BaP, IP, BkF, CH, BbF, and BaA were 1, 1, 0.1, 0.01, 0.001, 0.1, and 0.1, respectively. The TEQ in each station was estimated by the following equation (33,34):

$$\mathrm{TEQ} = \Sigma(\mathrm{TEF}_i * \mathrm{cPAH}_i) \qquad (1)$$

Where TEF_i is toxic equivalent factor for any cPAH and $cPAH_i$ is carcinogenic PAH values (ng/g dw).

Sediment quality guidelines (SQGs) and sediment quality criteria (SQC) have been used to measure the PAHs ecotoxicological effects in sediments. The SQGs standard contains two effect levels: Effect range low (ERL) and effect range median (ERM). If PAHs amounts are less than ERL, it means that the toxicity possibility and other effects are rare. If concentrations are equivalent or higher than the ERL and less than ERM, negative biological effects may be happening sporadically. Values equivalent to or higher than the ERM mean that a negative biological efficacy would happen frequently (35). The SQCs standard includes five effect levels including rare effect level (REL), threshold effect level (TEL), occasional effect level (OEL), probable effect level (PEL), and frequent effect level (FEL) (36).

Another method for assessing the possible ecotoxicological effect of single chemicals is calculating the mean ERM quotient (M-ERM-Q) for all PAHs. M-ERM-Q was calculated using Eq. (2):

$$\mathrm{M\text{-}ERM} - \mathrm{Q} = \frac{\Sigma\,(ci\,/\,ERMi)}{n} \qquad (2)$$

Where *Ci* is the amount of any PAHi, *ERMi* is ERM of any PAHi, and *n* is the number of PAHs.

The M-ERM-Q lower than 0.1, 0.11–0.51, 0.51–1.5, and more than 1.5 have ≤11% (low pollution), 25-30% (medium to low pollution), 46-53% (medium to high pollution), and ≥75% (high pollution) probability of toxicity, respectively (15).

Analysis of data

The data were analyzed using SPSS version 23 for Windows. The results were presented as the mean ± standard deviation. Statistical significant level was considered at $P < 0.05$. The following data were analyzed: (a) the values of each PAH; (b) 16 PAHs concentration; (c) the total carcinogenic PAHs (DA, BaP, IP, BkF, CH, BbF, and BaA).

Results

Analysis of PAHs

The PAHs concentrations in sediment samples of 20 stations are shown in Table 1. The ΣPAHs ranged from ND (all stations in Bushehr(to 49180 ng/g dw (4 stations in Asaluyeh) with a medium value of 6894.55 ± 14301.55 ng/g dw.

Figure 2 shows the composition profiles of PAHs in the sediments. Generally, PAHs compounds with 2 and 3 rings were dominant in the Asaloyeh, Kangan, Khark, and Emam Hasan sediments and included 71.85%, 56.12%, 71.15%, and 76.79% of ΣPAHs, respectively.

Source identification

In order to study the source of PAHs, the Pearson's correlation ratios of individual PAHs in 20 sediment samples of Bushehr province are illustrated in Table 2. Significant positive correlations were observed for several PAHs pairs: ACE-ACY, FL-ACY, FL-ACE, AN-ACY, AN-ACE, AN-FL, FLU-NA, FLU-PH, PY-ACY, PY-ACE, PY-FL, PY-AN, BkF-PH, BkF-FLU, BaP-NA, BaP-PH, BaP-BkF, IP-ACY, IP-ACE, IP-FL, IP-AN, IP-PY, DA-ACY, DA-ACE, DA-FL, DA-AN, DA-PY, and DA-IP. BaA, CH, BbF, and BP show no significant correlation with the other PAHs studied.

The other parameter used to identify the origins of PHAs is ΣLPAHs/ΣHPAHs ratio. According to Figure 2, ΣLPAHs/ΣHPAHs ratio at stations A$_1$, K$_1$, K$_3$, Kh$_1$, and B$_2$ was less than 1 and this ratio at other stations was higher than 1.

Figure 3 shows the values of PH/AN, AN/(PH + AN), and IP/(IP + BP). PH/AN and AN/(PH + AN) in all sites were lower than 10. IP/(IP + BP) in all sites were higher than 0.5.

Ecological risk assessment

According to Figure 2, PAHs compounds with 2 and 3 rings, which are LMW, are dominant in the Asaloyeh, Kangan, Khark, and Emam Hasan sediments. LMW PAHs (e.g., NA and FL) are toxic and non-carcinogenic for aquatic organisms; while several HMW PAHs (e.g., BaP and BbF) are mutagenic and carcinogenic to organisms like fish, birds, and mammals (37).

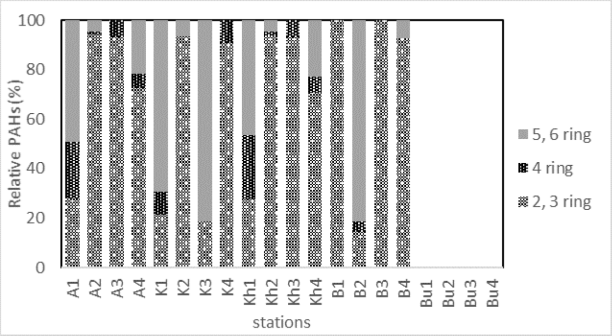

Figure 2. Percentage PAHs composition based on benzene ring in the sediment samples.

In this study, the toxicity of sediments was estimated based on the total quantity of the seven carcinogenic PAHs including CH, BbF, BaA, BaP, BkF, IP, and DA. As indicated in Table 1, the medium values of ΣCPAHs in sediment samples of 20 stations ranged from ND to 10690 ng/g, with a medium amount of 1629.37 ± 3541.39 ng/g dw. In addition, ΣCPAHs were 0% to 86% of ΣPAHs.

In this research, the total TEQ car levels of sediments ranged from ND to 7999 ngTEQ/g dw, with a medium amount of 804.77 ± 2338.80 ngTEQ/g dw. In addition, the mean of TEQ car values in the Asaluyeh, Kangan, Khark, Emam Hasan, and Bushehr stations were 1884.29, 36.32, 2069.02, 34.25, and ND ng TEQ/g dw, respectively (Table 1). In addition, higher amounts for total TEQ were reported compared to those reported by Qiao et al (38); on the other hand, Sprovieri et al (39) reported lower amounts.

The m-ERM-q amounts of PAHs in 20 stations are shown in Table 1. These values varied from ND to 7.414 with a mean value of 1.197 ± 2.42.

The comparative evaluation of the values of ERL and ERM (SQGs) for PAHs are presented in Table 3. In this study, the ΣPAH concentration in 60% of all sites was lower than ERL (rare negative effects), but 30% of all sites had a ΣPAHs concentration higher than ERL and lower than ERM (sporadically negative effects) and ΣPAHs concentration in 10% of all samples (related to Asalouyeh and Khark stations) were higher than the ERM (frequently

Table 1. Comparison of ΣPAHs (ng/g) in sediments of studied stations with other locations

Location	ΣPAHs	Contamination Level	References
Bushehr Province shores	ND - 49180	Low to very high	Present study
Daya Bay, China	42.5–158.2	Low	(45)
Khark Island, SW Iran	2.95–253.3	Low to moderate	(47)
Norwegian Harbor, Norway	2000–76 000	High to very high	(42)
Commercial ports from Spain	260–66,710	Moderate to very high	(41)
Intertidal zone, Yangtze Estuary, China	263–6372	Moderate to very high	(48)
Boston Harbor, USA	7300–358 000	Very high	(43)
Kaohsiung Harbor, Taiwan	472–16 207	Moderate to very high	(24)
Pearl River Delta, China	52.7–717	Low to moderate	(44)
Intertidal zone, Bohai Bay, Northeast China	37.2–206.6	Low to moderate	(49)

Table 2. Concentrations (ng/g dw) of PAHs in sediment samples collected from the sampling stations and effective parameters on the ecotoxicology effects of PAHs

	Stations	NA	ACY	ACE	FL	PH	AN	FLU	PY	BaA	CH	BbF	BkF	BaP	IP	DA	BP	TPAH (ng/g dw)	m-ERM-q	ΣCPAHs (ng/g dw)	TEQ (ngTEQ/g)
Asaluyeh	1	ND	ND	ND	ND	ND	160	ND	40	ND	90	ND	90	ND	90	100	ND	570	0.048	370	109.99
	2	5480	ND	ND	ND	50	160	50	40	ND	ND	ND	120	40	ND	110	ND	6050	0.271	270	151.2
	3	ND	ND	ND	1040	ND	140	ND	ND	90	ND	ND	ND	ND	ND	ND	ND	1270	0.175	90	9
	4	ND	13270	17050	1820	ND	3460	ND	2920	ND	ND	ND	ND	ND	3770	6890	ND	49180	7.414	10660	7267
	Aver	1370± 2740	3318± 6635	4263± 8525	±715 884.89	13± 25	±980 1653	13± 25	±750 1446.78	23± 45	23± 45	ND	±53 61.84	10± 20	±965 1870.48	±1775 3410.36	ND	14267± 23402.04	1.97± 3.62	2847.5± 5209.62	1884.29± 3588.96
Kangan	1	ND	ND	ND	ND	ND	140	ND	ND	ND	60	ND	110	ND	340	ND	ND	650	0.012	510	35.16
	2	ND	7700	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	540	ND	ND	8240	1.002	540	54
	3	ND	ND	ND	ND	30	140	ND	ND	ND	ND	ND	200	ND	540	ND	ND	910	0.012	740	56
	4	ND	ND	ND	1040	ND	150	ND	ND	ND	120	ND	ND	ND	ND	ND	ND	1310	0.175	120	0.12
	Aver	ND	1925± 3850	ND	260± 520	8± 15	±108 71.82	ND	ND	ND	±45 57.44	ND	±78 96.73	ND	±355 254.75	ND	ND	2777.50± 3651.77	0.30± 0.47	477.5± 259.27	36.32± 25.89
Khark	1	ND	ND	ND	ND	ND	159	ND	50	ND	100	ND	90	ND	60	120	ND	579	0.055	370	127
	2	4890	ND	ND	ND	50	140	50	45	ND	ND	ND	110	40	ND	100	ND	5425	0.243	250	141.1
	3	ND	ND	ND	1020	ND	150	ND	ND	90	ND	ND	ND	ND	ND	ND	ND	1260	0.173	90	9
	4	ND	13140	15060	1770	ND	3225	ND	3102	ND	ND	ND	ND	ND	2990	7700	ND	46987	7.305	10690	7999
	Aver	1223± 2445	3285± 6570	3765± 7530	±697 861.64	13± 25	±919 1537.68	13± 25	±799 1535.33	23± 45	25± 50	ND	±50 58.30	10± 20	±762 1485.26	±1980 3813.69	ND	13562.75± 22385.55	1.94± 3.57	2850± 5227.92	2069.02± 3953.76
Emam Hasan	1	ND	ND	4420	ND	ND	170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4590	0.749	ND	ND
	2	ND	ND	ND	ND	ND	170	ND	ND	50	ND	ND	ND	ND	960	ND	ND	1180	0.015	1010	101
	3	ND	ND	4520	ND	ND	200	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4720	0.763	ND	ND
	4	ND	ND	4460	ND	ND	150	ND	ND	ND	ND	ND	ND	ND	360	ND	ND	4970	0.754	360	36
	Aver	ND	ND	±3350 2233.71	ND	ND	±172 20.16	ND	ND	13± 25	ND	ND	ND	ND	±330 452.99	ND	ND	3865±1796.93	0.57±0.37	342.5±476.26	34.25±47.62
Bushehr	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Aver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not Detection.

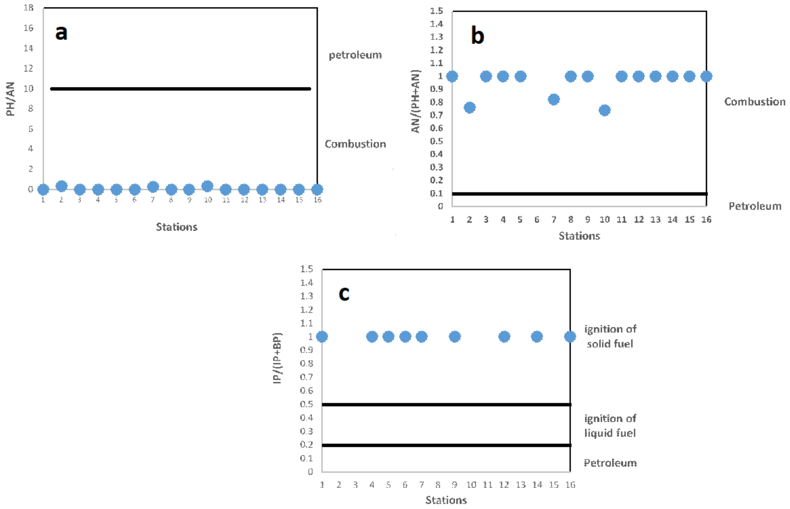

Figure 3. Plan of isomeric ratios of a) PH/AN, b) AN/PHAN, and c) IP/(IP+BP).

negative effects). In relation to the individual compounds, ERL values exceeded for AN and DA in 81.25% and 25% of all samples, respectively; but the ERM values exceeded for NA, AN, PY, and DA in 12.5%, for ACY in 18.75%, and for ACE and FL in 31.25% of all samples.

The findings presented in Figure 4 show that the amounts of 12 PAHs at 77.5% of the sites were lower than their corresponding REL values, and PAHs concentrations at 6% of all stations (including Asaluyeh and Khark stations) also exceeded FEL levels.

Discussion

Analysis of PAHs

According to Table 1 and based on the one-way ANOVA, the difference in the ΣPAHs between sediment samples in Bushehr province was not significant ($P>0.05$). The higher PAHs concentrations in sediments of Asaluyeh and Khark areas compared to other areas can be because of the discharge of sewage from gas and oil refineries, municipal sewage, oil leakages into the aquatic environments. The lower amounts of PAHs in Bushehr province stations may be related to stations far from harbors and municipal

Table 3. Pearson's correlation coefficient for PAH concentrations in sediments in Bushehr province

PAHs	PAHs															
	NA	ACY	ACE	FL	PH	AN	FLU	PY	BaA	CH	BbF	BkF	BaP	IP	DA	BP
NA	1															
ACY	-0.136	1														
ACE	-0.156	**0.851****	1													
FL	0.08	**0.707****	**0.717****	1												
PH	0.417	-0.167	-0.191	-0.225	1											
AN	-0.096	**0.903****	**0.952****	**0.807****	-0.121	1										
FLU	**0.475***	-0.136	-0.156	-0.183	**0.912****	-0.098	1									
PY	-0.107	**0.915****	**0.939****	**0.796****	-0.126	**0.995****	-0.090	1								
BaA	0.363	-0.166	-0.190	0.314	-0.166	-0.119	-0.135	-0.140	1							
CH	-0.161	-0.197	-0.226	0.002	-0.198	-0.141	-0.161	-0.154	-0.196	1						
BbF	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}					
BkF	0.155	-0.250	-0.287	-0.337	**0.687****	-0.181	**0.449***	-0.194	-0.249	0.231	0^{a}	1				
BaP	**0.475***	-0.136	-0.156	-0.183	**0.912****	-0.098	1.00	-.099	-0.135	-0.161	0^{a}	**0.449***	1			
IP	-0160	**0.915****	**0.908****	**0.728****	-0.145	**0.963****	-0.160	**0.954****	-0.10	-0.187	0^{a}	-0.160	-0.160	1		
DA	-0.105	**0.913****	**0.937****	**0.795****	-0.125	**0.993****	-0.099	**1.000****	-0.139	-0.154	0^{a}	-0.194	-0.099	**0.949****	1	
BP	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}	0^{a}

*Relationship is significant at the 0.05 level.
**Relationship is significant at the 0.01 level (2-tailed).
^{a} Cannot be calculated because at least one of the variables is constant.

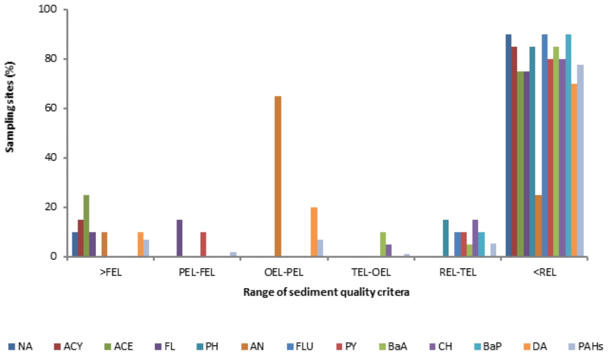

Figure 4. PAHs risk evaluation based on the sediment quality criteria in Canada.

regions and the lack of direct evacuations.

PAHs is classified into four groups including low (0–100 ng/g), medium (100–1000 ng/g), high (1000–5000 ng/g), and very high (>5000 ng/g) pollution (40). Accordingly, sediments from Bushehr province shores can be classified as low to very highly contaminated by PAHs.

The PAHs contamination levels at sediment samples of Bushehr province shores are consistent with the results reported by Chen and Chen (24) and Casado-Martínez et al (41) but are less than those reported in the Norwegian harbor in Norway (42) and Boston port in the USA (43). However, higher levels of PAHs contamination in sediment samples were reported compared to those reported by Wang et al (44) and Yan et al (45) (Table 4). The differences in values of PAHs at different areas sediments around the world may be due to the differences in PAHs compounds, geological features of sampling stations and source of contamination. In addition, tides can also be effective in the distribution of PAHs.

Source identification

According to Table 2, individual PAHs that have significant positive correlations, may be originated from common anthropogenic sources, but can be originated from another source except for local anthropological sources for individual PAHs with no significant positive association.

The main PAHs sources at coastal sediments include combustion processes (pyrogenic sources) and petroleum products (petrogenic sources) (46). In the studied area, the origin of PAHs at stations A_1, K_1, K_3, Kh_1, and B_2 is pyrogenic and the origin of PAHs at the rest of the stations is petrogenic as ΣLPAHs/ΣHPAHs ratios at stations A_1, K_1, K_3, Kh_1, and B_2 were less than 1 while the ratios were reported to be higher than 1 at other stations (Figure 2).

As shown in Figure 3, the values of PH/AN in all sites were lower than 10, indicating that pyrogenic sources played a major role in sediment pollution. In this study, the results of the ratios of AN/(PH + AN) were similar to the results of PH/AN ratios. Accordingly, the IP/(IP + BP) in all sites were more than 0.5, indicating that pyrogenic sources are dominant (Figure 3).

In conclusion, the three ratios of AN/(AN + PH), FLU/(FLU + PY), and CH/(BaA + CH) present similar findings. Pyrogenic PAHs were predominant in the studied area samples, which can be caused by diesel engine output. Furthermore, traffic and coal burning can increase the PAHs values through rainfalls and runoff. Based on the ΣLPAHs/ΣHPAHs ratio, in some areas, petrogenic sources may help PAHs pollutions, which could originate from oil/diesel/gas leakages and oily effluent discharge.

Ecological risk assessment

The m-ERM-q amounts of PAHs in Table 1 show that Bushehr stations are categorized as a low group (≤ 11% probability of toxicity), Kangan stations as a medium-low group (25%-30% probability of toxicity), Emam Hasan station as a medium-high group (46%-53% probability of toxicity), and Asaluyeh and Khark stations as high priority groups (≥75% probability of toxicity).

According to the values of ERL and ERM (SQGs) for PAHs presented in Table 5, it was revealed that some sites perhaps have single PAHs that sporadically and frequently cause negative ecotoxicological risk effects.

The SQCs are based on SQGs according to technical, natural, social, economic conditions and etc. In the present study, PAHs pollution levels were evaluated based on the standard SQC values in Canada (Table 5) (36). These values can be employed in the management of environmental such as recovery, dragging, and contamination control.

The findings show that the amounts of 12 PAHs at 77.5% of the sites were lower than their corresponding

Table 4. The percentage of ERL and ERM (SQGs) for PAHs in the sediment samples

PAHs	(ng/g dw) SQGs: ERL-ERM	SQGs		
		<ERL (%)	ERL-ERM (%)	>ERM (%)
NA	160-2100	90	-	10
ACY	44-640	85	-	15
ACE	16-500	75	-	25
FL	19-540	75	-	25
PH	240-1500	100	-	-
AN	85.3-1100	25	65	10
FLU	600-5100	100	-	-
PY	660-2600	90	-	10
BaA	261-1600	100	-	-
CH	384-2800	100	-	-
BbF	-	-	-	-
BbK	-	-	-	-
BaP	430-1600	100	-	-
IP	-	-	-	-
DA	63.4-260	70	20	10
BP	-	-	-	-
PAHsΣ	4022-44792	60	30	10

Table 5. Evaluation criteria of coastal sediment quality for PAHs in Canada (ng/g)

PAH	REL	TEL	OEL	PEL	FEL
NA	17	35	120	390	1200
ACY	3.3	5.9	31	130	340
ACE	3.7	6.7	21	89	940
FL	10	21	61	140	1200
PH	23	87	250	540	2100
AN	16	47	110	240	1100
FLU	27	110	500	1500	4200
PY	41	150	420	1400	3800
BaA	27	75	280	690	1900
CH	37	110	300	850	2200
BbF	-	-	-	-	-
BbK	-	-	-	-	-
BaP	34	89	230	760	1700
IP	-	-	-	-	-
DA	3.3	6.2	43	140	200
BP	-	-	-	-	-

REL values, indicating that harmful PAHs effects in these areas are rare (Figure 4). PAHs concentrations at 6% of all stations (including Asaluyeh and Khark stations) also exceeded FEL levels, indicating that negative effects of PAH compounds in these areas occur frequently (Figure 4). So now, further evaluation on the environmental risks of PAHs compounds in these areas is required because there is low surface sediment that needs to be corrected.

Conclusion

In this study, considerable information on the distribution, probable origin, and ecotoxicology efficacy of PAHs in the surface sediments from Bushehr Province shores are presented. The levels of PAHs in sediments from sampling sites are low to very high. In stations of A1, K1, K3, Kh1, and B2, 4-6-ring PAHs were abundant in sediments, whereas, ΣLPAHs/ΣHPAHs ratios at other stations were higher than 1. Based on the three PAHs isomeric ratios, the pollutants of sediments were originated from combustion processes (pyrogenic sources). In relation to the ecotoxicological assessment, ΣPAHs concentration and several single PAHs in some sites exceeded ERM, indicating frequent negative effects of ecotoxicological risk. The findings of biological effect evaluation showed that coastal sediments of Bushehr province shores have 11% (Bushehr stations) to 75% (Asaluyeh and Khark stations) probability of toxicity. The SQC also indicated that the possibility of negative effects of 12 PAHs composition is low. Nevertheless, toxic effects related to NA, ACY, ACE, FL, AN, and DA would occur frequently in Asaluyeh and Khark stations. Therefore, station sediments must be routinely sampled for PAHs because PAHs may have a negative effect on the marine ecosystems, organisms, and humans.

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Ethical issues

Not applicable.

Competing interests

The authors declare that they have no conflict of interests.

Author's contributions

GN performed experiments and drafted the manuscript. NJ, TT, EK, and ARP reviewed the manuscript. All authors contributed to the critical reading and discussion of the manuscript. All authors have read and approved the published version of the manuscript.

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