Polycyclic aromatic hydrocarbons (PAHs) in coastal sediments from urban and industrial areas of Asaluyeh Harbor, Iran: distribution, potential source and ecological risk assessment

Alireza Raeisi, Hossein Arfaeinia, Morteza Seifi, Mehdi Shirzad-Siboni, Mozhgan Keshtkar and Sina Dobaradaran

ABSTRACT

The distribution and toxicity levels of 16 EPA priority pollutant polycyclic aromatic hydrocarbons (PAHs) in the sediments of Asaluyeh shore, Iran were investigated. The total concentrations of the PAHs in surface sediments ranged from 1,054 to 17,448 ng/g dry weights with a mean concentration of 8,067 ng/g. The spatial distribution of PAHs showed that PAH levels are much higher in the industrial areas in comparison with urban areas. Based on diagnostic ratios, pyrogenic activities were dominant sources of PAHs pollution in sediments comparing petroleum sources. The toxic equivalent concentrations (TEQ Carc) of PAHs ranged from 172 to 2,235 ng TEQ/g with mean value of 997.9. Toxicity levels were evaluated using sediment quality guidelines (SQGs) and toxic equivalent factors. Samples were collected from industrial and urban stations in Asaluyeh shores. According to SQGs, ΣPAHs concentrations in sediments of urban areas were below the ERL (effects range low), but the industrial samples had ΣPAHs concentrations between ERL and ERM (effects range median). Furthermore, ΣHPAHs (heavy PAHs) and some individual PAHs in some industrial stations exceeded ERM, indicating adverse ecological risk effects frequently occur. Findings demonstrate that the surface sediment from Asaluyeh shore is highly to very highly contaminated with PAHs.

Key words | polycyclic aromatic hydrocarbons (PAHs), risk assessment, sediment, sediment quality guidelines (SQGs), toxic equivalent concentrations (TEQ Carc)

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental pollutants generated by pyrolysis or incomplete combustion of organic materials, and consist of diverse groups of organic compounds (Menzie *et al.* 1992). The general structure of PAHs comprise two or more condensed aromatic rings arranged in various structural configurations (Liu *et al.* 2007). The PAHs that consist of fused aromatic rings containing up to four fused benzene rings are called light PAHs (LPAHS), and those consisting of more than four benzene rings are known as heavy PAHs (HPAHs). HPAHs are more toxic and more stable than the light ones (Wenzl *et al.* 2006).

Particular attention has been paid to PAH components due to their mutagenic and carcinogenic effects on humans (Man *et al.* 2013). Hence, PAHs have been included in the Environmental Protection Agency (EPA) and the European Commission priority pollutant lists (EPA 1993; European Commission 2011). Like chlorinated aliphatic hydrocarbons (Dobaradaran *et al.* 2010), PAH compounds can be present in the atmosphere, water, sediments, tobacco smoke and food (Wang *et al.* 2001; Yan *et al.* 2009). They may be emitted into the surroundings by natural processes and anthropogenic activities, but the latter is considered to be the main source of PAHs input into the environment (Zhou *et al.* 1998; Chen & Chen 2011).

PAHs are present in the marine environment where they are linked with petrogenic, pyrolytic and diagenetic sources. The input route of PAHs to coastal water could be direct (e.g. continental runoff, sewage outflows and direct oil spills) or indirect (e.g. air–sea gas exchange and atmospheric deposition). A series of processes (e.g. volatilization, deposition, sinking, degradation and resuspension) determines the ultimate content of PAHs in the marine environment (Guitart *et al.* 2010). PAHs compounds are hydrophobic with low water solubility and, thus, their concentrations in water are at low levels (Karcher 1988) because they tend to be absorbed by water-borne organic and inorganic particles. PAHs can be ultimately deposited and persist in sediment and aquatic marine ecosystems. In addition, the PAHs found in the bed sediment are resistant to bacterial degradation in an anoxic environment. Under favorable environmental conditions, deposited PAHs may be released into the water as a continuing source that threaten aquatic ecosystems by bioaccumulation in the food chain (Chen & Chen 2011).

Asaluyeh is a city in and the capital of Asaluyeh County, in Bushehr Province, Iran. Asaluyeh is located on the shores of the Persian Gulf some 270 km southeast of the provincial capital of Bushehr. It is best known as the site for the land based facilities of the huge PSEEZ (Pars Special Energy Economic Zone) project. The PSEEZ has been allocated 100 km^2 of land at Asaluyeh for the various complexes and facilities. The site is a collection of different petrochemical industries and refineries and is administered by the PSEEZ agency onsite. Rapid industrial development in the previous two decades, and especially the rapid increase of petrochemical industries, have led to serious concerns about environmental pollution (Arfaeinia *et al.* 2016). However, there is no information about pollution in Asaluyeh sediments.

The main objectives of this study were to: (1) determine the distribution, composition, and relative pollution levels of PAHs in industrial and urban sediments of Asaluyeh shore; (2) identify possible sources of PAHs; and (3) investigate the potential biological and toxicological effects on the environment.

MATERIALS AND METHODS

Sampling

Sediments used in this work were collected from 12 stations in urban and industrial areas (Figure 1). Sampling stations were chosen to ensure that samples would be representative and cover the whole shore water, be evenly distributed, and represent possible pollution sources so that a general evaluation of pollution levels of sediment could be effectively carried out. Onsite sampling of all 12 surface sediments was carried out during four months from September to December 2014, in Asaluyeh Harbor. Using the global positioning system, precise stations for each sampling point were identified. Surface sediments were collected using an Ekman steel grab sampler ($25 \times 25 \times 25$ cm^3). Sediment samples, from each station, were first mixed thoroughly and stored in glass jars, which had been pre-washed and stored in an icebox, then brought back to the laboratory for analysis. In the laboratory, sediments were freeze-dried for 48 h, then wet sieved (<0.5 mm) and homogenized completely. The dried samples were stored at $-20\ {}^\circ$C in amber glass bottles which were pre-washed with n-hexane and covered with solvent-rinsed aluminum foil for analysis.
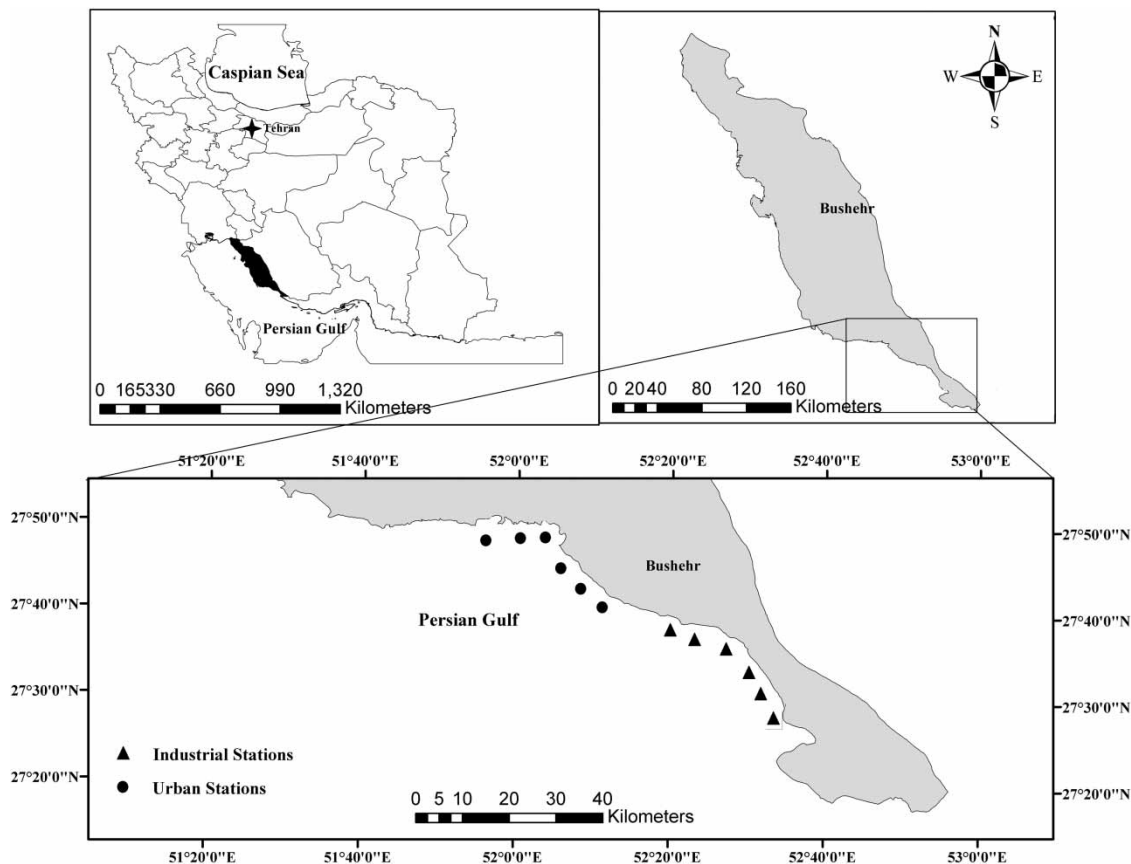
Figure 1 | Map of sampling stations.

Chemicals

Standards of 16 PAHs were obtained from Merck (Darmstadt, Germany) including naphthalene (NA), acenaphthene (ACE), acenaphthylene (ACY), phenanthrene (PH), fluorene (FL), anthracene (AN), pyrene (PY), fluoranthene (FLU), benzo[a]anthracene (BaA), chrysene (CH), benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), benzo[k]fluoranthene (BkF), indeno[1,2,3-cd]pyrene (IP), and benzobenzo[g,h,i]perylene (BP), dibenzo[a,h]anthracene (DA), dichloromethane, n-hexane and other solvents of spectral purity level (United States World Company).

Sample preparation and analysis

Sediment size separation was carried out with a Coulter LS Particle Size Analyzer as reported by (Hung & Hsu 2004; Chen *et al.* 2007). Three operational size fractions (>75 μm, 2–75 μm, <2 μm) labeled as sand, silt and clay, respectively, were used to fraction each sediment sample. Wet sediment samples were heated in an oven at 105 °C

and at a constant weight. With respect to weight difference before and after heating, the water content of each sample was calculated. The dry sediments were heated again to 550 °C, and the weight difference before and after heating was considered as organic matter (APHA 2001).

For the PAH analysis, 10 g of each sample were mixed with 250 mL of n-hexane:dichloromethane (1:1, v/v), then the mixture was put in Soxhlet for 8 h. The combined extract was evaporated on a rotary vacuum evaporator until 15 mL remained. To remove sulphur and their compounds, activated copper was added and passed through a filter paper (Whatman GF/ C, 24 micron) for 24 h. The extract was concentrated in a rotary (Buchi B-490) to 5 mL. The extract was passed through a column containing 10 g alumina, 2 g anhydrous sodium sulphate, and 10 g silica gel in n-hexane. Thereafter, 30 mL of a mixture of dichloromethane:n-hexane (9:1, v/v) was added. The mixture was concentrated again to 5 mL. The extract was dried using a gentle stream of nitrogen (N-E VAP 112, USA). The residue was dissolved in 1 mL of acetonitrile (MOOPAM 1999).

A high performance liquid chromatographer (HPLC) (Waters 510, Milford, MA) equipped with a fluorescence detector (Waters 470) and autosampler (Waters 717) was used to detect the PAHs. The column type was RESTEK, Pinacle II PAH (150 × 3.2 mm, 5 μm) and the column temperature was set at 25 °C. Injection volume was 20 μL. The initial mobile phase was HPLC grade water: acetonitrile (1:1, v/v) for 7 min, which was gradually changed to 100% acetonitrile in 6 min, held at 100% for 20 min, then decreased to initial phase. Identification and determination of PAHs was standardized by the peak areas and retention times of the calibration standards.

Quality assurance

All data in this study were obtained under strict control procedures and quality assurances. Spiked blanks, laboratory blanks and replicate samples were tested together with the sediment samples. The recovery rate ranged from 81 to 94% with a relative standard deviation of 3–9%. To monitor the quality control, procedural blanks were analyzed with every five samples. PAHs were not detected in any of the analytical blanks. Quantitative analysis was carried out on a five-point linear calibration of PAH solution, acquired by dilution of the 16-PAH mixture. Limit of detection was measured with a signal-to-noise ratio (S/N) of 3. The method detection limit were between 0.1 and 1 ng/g. Satisfactory linearity was obtained with values of the correlation coefficient R above 0.99.

Data analysis

The results obtained were statistically analyzed using SPSS for Windows version 18 (SPSS Inc., Chicago, IL, USA). Data analyses, including mean, maximum and minimum concentrations, and standard deviation, were performed. A regression model was applied to test the relationship between sediment characteristics and PAH concentrations. The following data were analyzed: (a) the concentration of each PAH; (b) 16 PAHs; (c) the total of six PAHs with low molecular weight (ACY, NA, FL, ACE, PH, and AN); (d) 10 PAHs with high molecular weight (PY, FLU, BaA, CH, BkF, BbF, BaP, B, DA, and IP); and (e) potential carcinogenic PAHs (BaA, BbF, CH, BkF, IP, BaP, and DA).

ΣCPAHs (carcinogenic PAHs) including BaA, CH, BbF, BkF, BaP, IP, and DA according to (EPA 1993), were used to calculate benzo[a]pyrene equivalents. The toxic equivalency factors (TEFs), the toxic factor of carcinogenic PAHs relative to benzo[a]pyrene (BaP), adopted by the EPA (1993), was calculated to assess sediment toxicity. The TEFs

provided values for BaA = 0.1, CH = 0.001, BbF = 0.1, BkF = 0.01, BaP = 1, DA = 1, and IP = 0.1.

Sediment quality guidelines (SQGs) are an important issue and a significant tool for the evaluation of pollution effects on aquatic systems. In this study, SQGs were used to investigate the ecological and biological toxicity of PAHs concentrations in sediments (Long *et al.* 1998; Zeng *et al.* 2008). The US National Oceanic and Atmospheric Administration provide a sediment toxicity screening guideline which includes two target values to estimate potential biological effects: effects range low (ERL) and effects range median (ERM) (Long *et al.* 1995). These two values delineate three concentration ranges for each particular chemical. When the concentration of an environmental contaminant is below the ERL, it indicates that the biological effect is rare. If concentration equals to or is greater than the ERL, but below the ERM, it indicates that a biological effect would occur occasionally. Concentrations at or above the ERM indicate that a negative biological effect would frequently occur (Long *et al.* 1995).

Another approach to evaluate possible ecotoxicological effects of individual chemicals, by comparing the chemical concentrations with the limit concentrations, is the mean ERM quotient (m-ERM-q), which calculates the mean quotient for all PAHs. Based on Long *et al.* (1998, 2000) the mean ERM quotient (m- ERM-q) has been calculated using the following equation:

$$M - ERM - Q = \frac{\Sigma(C_i/ERM_i)}{n}$$

where C_i is the sediment concentration of compound i, ERM_i is the ERM value for compound i and n is the number of compounds. The m-ERM-q has been associated with the probability of toxicity, according to the matching of chemical and toxicity data from the US estuaries (Long *et al.* 1998, 2000). The m-ERM-q can be classified into four groups including lower than 0.1, 0.11 to 0.51, 0.51 to 1.5 and more than 1.5 which represent 11%, 30%, 46% and 75% probability of toxicity, respectively (Long *et al.* 2000). Additionally, the above-mentioned groups can also categorize the stations as low, medium-low, medium-high and high priority sites, respectively (Chen *et al.* 2013).

RESULTS AND DISCUSSION

Concentrations and distribution of PAHs

The organic matter contents and grain size (sand, silt and clay) distribution in sediment samples are shown in

Table 1 │ Stations, depth, grain size (sand, silt, and clay) and organic matter content of sediments in Asaluyeh shores

Stations	Latitude (°N)	Longitude (°E)	Water depth (m)	Clay (%)	Silt (%)	Sand (%)	Organic matter (%)
1	27°40′39.1″	52°16′29.4″	6.7	12.5	60.4	27.1	7.4
2	27°41′01.8″	52°14′50.9″	7.8	13.4	74.3	12.3	9.3
3	27°41′19.9″	52°13′49.1″	9.3	8.2	58.6	33.2	11.1
4	27°43′12.6″	52°10′48.7″	13.2	14.8	55.2	30	10.6
5	27°44′33.6″	52°09′03.2″	7.4	9.4	76.4	14.2	8.1
6	27°45′27.8″	52°07′54.0″	12.1	7.6	69.1	23.3	7.7
Mean of urban stations	–	–	9.4 ± 2.6	10.9 ± 2.9	65.6 ± 8.8	23.3 ± 8.4	9 ± 1.5
7	27°49′47.8″	52°03′16.4″	11.3	8.5	64.9	26.6	11.8
8	27°50′12.4″	52°02′54.1″	8.2	16.8	53.2	30	14.3
9	27°50′06.4″	51°58′31.8″	6.4	10.7	67.5	21.8	16.2
10	27°50′04.3″	51°56′47.7″	10.5	9.1	61.4	29.5	15.8
11	27°49′51.2″	51°56′13.4″	11.7	6.4	65.1	28.5	12.4
12	27°49′36.6″	51°55′29.5″	7.4	12.6	74.9	12.5	9.6
Mean of industrial stations	–	–	9.2 ± 2.2	10.6 ± 3.6	64.5 ± 7.1	24.8 ± 6.7	13.3 ± 2.5
Mean of all stations	–	–	9.3 ± 2.3	10.8 ± 3.1	65 ± 7.6	24 ± 7.3	11.1 ± 3.0

Table 1. The mean value of grain size analyzed in 12 stations showed that the silt fraction represented 65% of total mass, followed by 24% sand and 10.8% clay. There were no significant differences between grain size sediment samples between urban and industrial stations.

As shown in Figure 2, the organic matter contents in industrial sediment were generally higher than in urban sediment. Total organic matter is one important factor that influences the PAHs levels in the sediments (Kim *et al.* 1999). Total organic matter content in sediment ranged from 7.4 to 16.2% which revealed the lowest and highest amount in stations 1 and 9, respectively. The mean organic matter content of industrial sediment samples was higher than in urban areas.

A regression model was used to compare the relationship between ΣPAHs content and organic matter. ΣPAHs concentrations were log transformed for this analysis. Organic matter content and ΣPAHs associated significantly ($P<0.05$) in 12 sampling stations according to the regression model. (Kim *et al.* 1999; Wang *et al.* 2001) pointed out that organic matter content can affect the PAHs distribution in sediments. In addition, some studies reported that there is a positive correlation between matter content and PAHs concentration in sediments (Yang 2000; Wang *et al.* 2001; De Luca *et al.* 2005). This was expected as it is well documented that hydrophobic organic substances will be mainly sorbed into particles through partition, which is in correlation with content of organic carbon (Zhou *et al.* 1998; Chiou 2002). Our findings show that the organic

matter content of sediment can influence the PAH distribution in sediments.

Marin *et al.* (2008) proposed a classification of ecological quality status concerning organic matter content into three levels: high-good (lower than 5%), moderate (5% to 10%) and poor-bad (higher than 10%). As shown in Table 1, stations 1, 2, 5, 6 and 12 indicated moderate qualities while other the stations (3, 4, 7, 8, 9, 10 and 11) are classified as poor-bad. The abundant organic content of the sediment reveal that the organic accumulation would lead to the notable variations in sediment characteristics. The sediments with high organic matter content have a strong tendency for hydrophobic components, such as PAHs (Macrae & Hall 1998; Xia & Wang 2008). The high organic properties of the sediment could cause a reduction in oxygen so that anaerobic and unhealthy conditions would occur in sediments (Chen *et al.* 2013).

The PAHs concentration in sediment samples of the 12 stations are shown in Tables 2 and 3 and in Figure 3. The amounts of total PAHs (ΣPAHs) ranged from 1,054 to 17,448 ng/g dw (dry weight) with an average value of 8,063 ± 7,311 ng/g dw. The ΣPAHs in the industrial and urban stations averaged 14,953 ± 1,814 and 1,182 ± 87 ng/g, respectively. This shows that the industrial zone represents the main source of sediment PAHs.

Sediment PAHs composition of 12 stations from the Asaluyeh shores are presented in Figures 4 and 5. 16 PAHs components were categorized into three groups: (a) 2-, 3-ring,
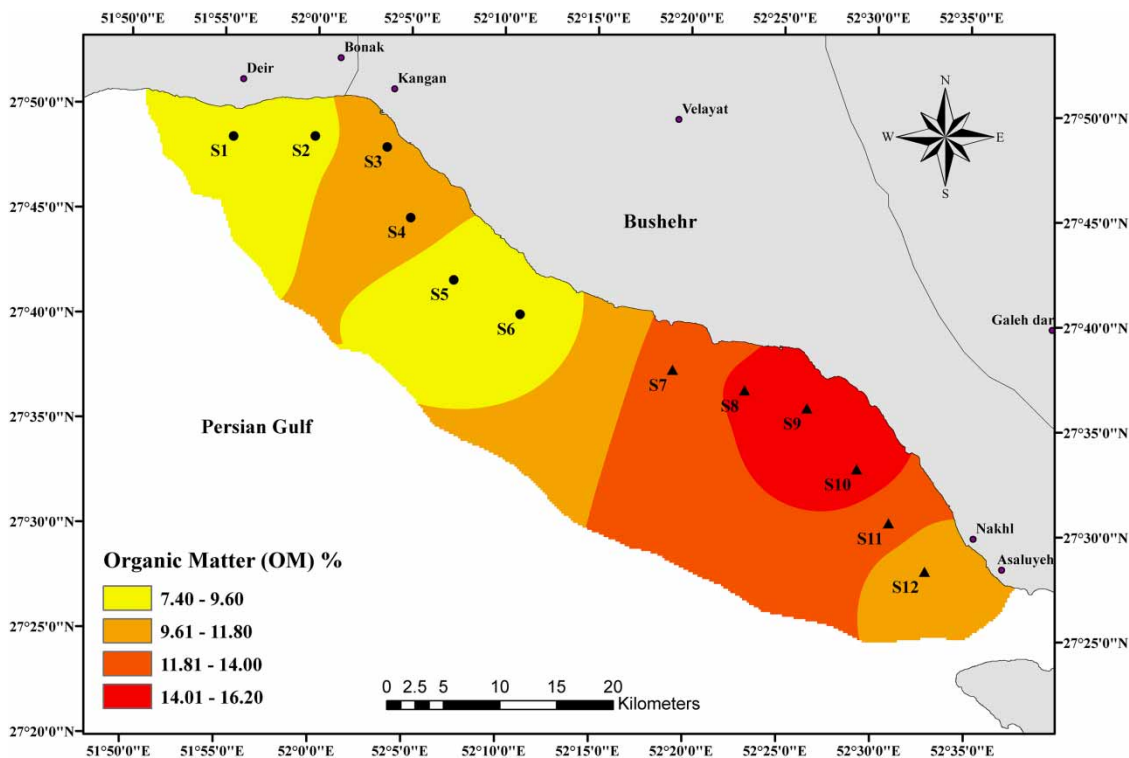
Figure 2 │ Comparison of organic matter content among sediments samples collected from Asaluyeh shore.

(b) 4-ring, and (c) 5-, 6-ring PAHs. In four stations (1, 3, 7, and 8) 5- and 6-ring PAHs were most abundant whereas in stations 2, 4, 9, 10, 11 and 12 the 4-ring PAHs were highest. The overall levels of 2- and 3-ring PAHs were low, except in station 7. High-molecular-weight PAHs commonly predominated in sediment samples. The higher levels of high-molecular-weight in comparison with low-molecular weight PAHs has been reported in sediments from marine and river environments (Magi *et al.* 2002; Guo *et al.* 2007).

Factors, including differences in type and number of PAH compounds tested, geological features of sampling stations, and sediments fractioned, make it difficult to compare the PAHs values studied in different areas around the world. Although, a general knowledge of other sediment contamination would be helpful. PAHs concentrations in sediments in various locations around the world are indicated in Table 4.

Baumard *et al.* (1998) proposed a classification of PAH contamination and categorized ΣPAHs into four groups including: low (0–100 ng/g), moderate (100–1,000 ng/g), high (1,000–5,000 ng/g), and very high (>5,000 ng/g). Accordingly, sediments from Asaluyeh shore can be specified as high (stations 1–6) to very high (station 7–12) for PAH contamination.

A comparison between PAH concentrations in sediments from different studies is shown in Table 4. The PAH concentrations in surface sediment from Asaluyeh shore, in this study, are similar to those found at Gemlik Bay in Turkey (Ünlü & Alpar 2006), Genoa-Voltri Harbor in Italy (Salvo *et al.* 2005), Kaohsiung Harbor in Taiwan (Chen *et al.* 2013), and Lazaret Bay in France (Baumard *et al.* 1998), but lower than those detected in the Norwegian Harbour in Norway (Oen *et al.* 2006), Boston Harbor in the USA (Wang *et al.* 2001), and Xiamen Harbour in China (Hong *et al.* 1995). However, the levels were significantly higher than those found at the Pearl River Delta in China (Wang *et al.* 2010), Daya Bay in China (Yan *et al.* 2009), Olbia Harbor in Italy (De Luca *et al.* 2005) and Incheon Harbor in Korea (Kim *et al.* 1999). As shown in Table 2, industrial stations have much higher levels of PAHs in comparison with urban sampling stations.

Sources of PAHs from Asaluyeh shore

There are two main sources of anthropogenic PAHs including combustion processes (pyrogenic sources) and leakage of noncombusted petroleum products (petrogenic sources) (Zakaria *et al.* 2002; Boonyatumanond *et al.* 2006).

Table 2 | Measured concentrations (ng/g dw) of PAHs for sediments samples collected from Asaluyeh shore

Station		NA	ACY	ACE	FL	PH	AN	FLU	PY	BaA	CH	BbF	BkF	BaP	IP	DA	BP
Urban	1	79	11	13	9	28	4.7	145	128	83	63	201	132	134	23	43	19
	2	68	7.4	9.6	21	22	2.8	173	184	98	113	167	98	108	15	36	35
	3	70	8.7	8.9	13	27	3.4	111	98	110	54	234	117	97	8.9	69	13
	4	57	14	5.4	6.8	45	2.7	210	194	131	63	114	84	123	19	54	15
	5	38	8.3	19	27	17	1.9	148	112	173	125	268	158	91	26	33	43
	6	86	16	15	15	39	4.7	243	189	80	49	179	101	169	13	47	32
Mean of urban stations		66.3 ± 17	10.9 ± 3.4	11.8 ± 4.8	15.3 ± 7.5	29.6 ± 10.5	3.3 ± 1.1	171.6 ± 47	150.8 ± 42	112.5 ± 35	77.8 ± 32	193.8 ± 53	115.0 ± 26	120.3 ± 28	17.4 ± 6.4	47.0 ± 13	26.1 ± 12
Industrial	7	1,539	179	661	437	1,512	195	1,742	998	934	738	1,471	1,439	998	238	116	441
	8	1,928	68	329	359	930	103	1,334	1,529	745	962	1,023	1,783	1,431	543	129	287
	9	2,004	93	438	674	1,630	239	2,145	1,739	1,821	1,023	1,517	1,695	1,243	349	257	563
	10	1,348	56	373	593	1,156	98	2,234	2,431	1,321	673	1,714	1,979	1,764	547	92	419
	11	890	173.4	540	180.7	1,330	194	1,590	1,129	984	1,327	871	1,378	1,065	412	143	349
	12	2,338	45	213	246	1,278	207	1,981	1,764	1,290	971	1,921	1,042	1,398	614	203	193
Mean of industrial stations		1,674.5 ± 520	102.4 ± 59	425.6 ± 158	414.9 ± 192	1,306.0 ± 250	172.6 ± 58	1,837.6 ± 345	1,598.3 ± 514	1,182.5 ± 382	868.2 ± 232	1,419.5 ± 402	1,552.6 ± 26	1,316.5 ± 279	435.0 ± 125	156.6 ± 61	384.0 ± 115
	ERL[a]	160	44	16	19	240	85.3	600	660	261	384	–	–	430	–	63.4	–
	ERM[a]	2,100	640	500	540	1,500	1,100	5,100	2,600	1,600	2,800	–	–	1,600	–	260	–

[a]ERL and ERM refers to the ERL and median (Long *et al.* 1995).

Table 3 | PAHs concentrations (ng/g dw) and diagnostic ratios in sediments of Asaluyeh shore

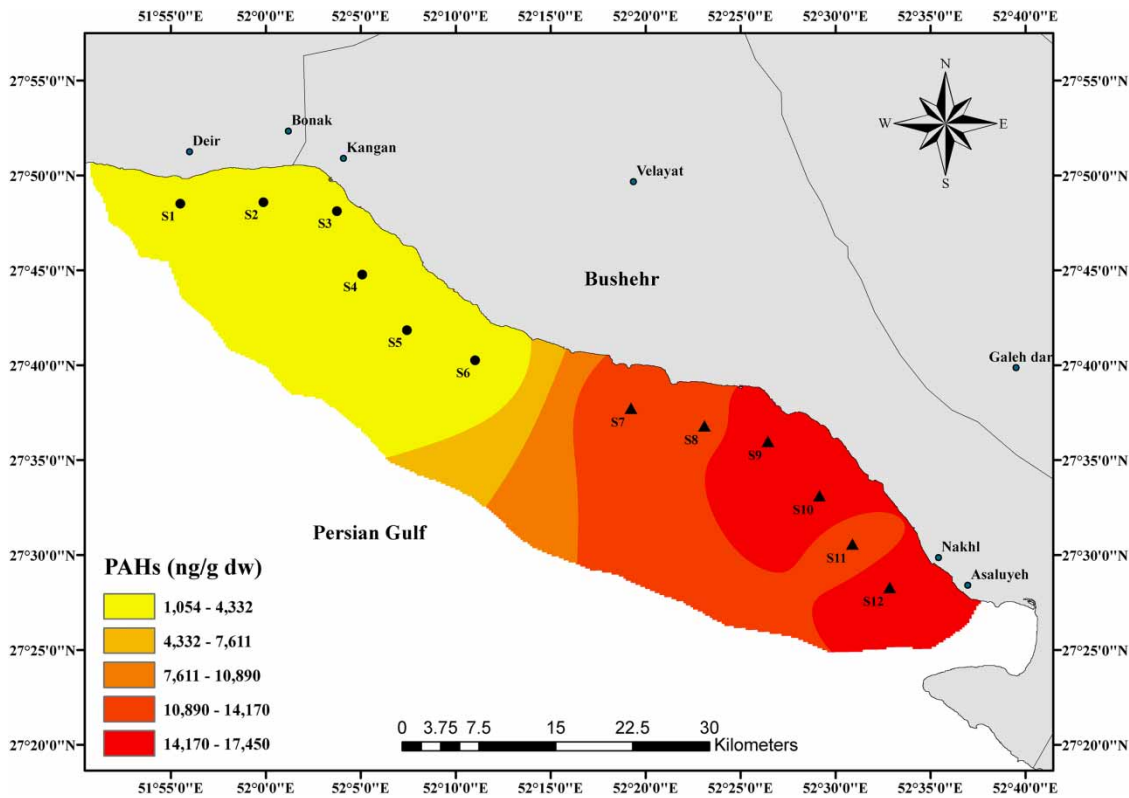| Station	ΣPAHs	ΣLPAHs	ΣHPAHs	ΣCPAHs	ΣLPAHs/ ΣHPAHs	PH/AN	AN/PH + AN	FLU/PY	FLU/ FLU + PY	IP/BP	m-ERM-q (ΣPAHs)	ΣCPAHs/ ΣPAHs	TEQ Carc
1	1,125	145	971	679.1	0.15	5.96	0.14	1.13	0.53	1.21	0.043	0.60	209
2	1,168	131	1,027	635.1	0.13	7.86	0.11	0.94	0.48	0.43	0.044	0.54	173
3	1,054	131	912	690.0	0.14	7.94	0.11	1.13	0.53	0.68	0.049	0.65	203
4	1,158	131	1,007	588.1	0.13	16.67	0.06	1.08	0.52	1.27	0.051	0.51	204
5	1,300	111	1,177	874.2	0.09	8.95	0.10	1.32	0.57	0.60	0.045	0.67	172
6	1,289	176	1,102	638.1	0.16	8.30	0.11	1.29	0.56	0.41	0.052	0.50	244
Mean of urban stations	1182.4 ± 95	137.5 ± 21	1032.6 ± 94	684.1 ± 99	0.13 ± 0.02	9.28 ± 3.7	0.11 ± 0.03	1.15 ± 0.14	0.53 ± 0.03	0.77 ± 0.38	0.047 ± 0.003	0.58 ± 0.08	201 ± 26.6
7	13,656	4,527	9,115	5,935.4	0.50	7.75	0.11	1.75	0.64	0.54	0.581	0.43	1,393
8	13,501	3,720	9,766	6,617.7	0.38	9.03	0.10	0.87	0.47	1.89	0.509	0.49	1,810
9	17,448	5,082	12,352	7,907.2	0.41	6.82	0.13	1.23	0.55	0.62	0.740	0.45	1,887
10	16,820	3,627	13,174	8,092.1	0.28	11.80	0.08	0.92	0.48	1.31	0.611	0.48	2,235
11	12,572	3,311	9,248	6,181.7	0.36	6.86	0.13	1.41	0.58	1.18	0.519	0.49	1,450
12	15,722	4,329	11,377	7,348.0	0.38	6.17	0.14	1.12	0.53	3.18	0.582	0.47	1,995
Mean of industrial stations	14,946 ± 1,984	4,099 ± 661	10,831 ± 1,711	7,013.7 ± 903	0.38 ± 0.07	8.07 ± 2.0	0.11 ± 0.02	1.22 ± 0.33	0.54 ± 0.03	1.28 ± 0.65	0.590 ± 0.08	0.47 ± 0.02	1,793 ± 322
ERL	4,022	552	1,700	–	–	–	–	–	–	–	–	–	–
ERM	44,792	3,160	9,600	–	–	–	–	–	–	–	–	–	–

Figure 3 | Total PAHs contents in sediment samples of 12 stations from Asaluyeh shore.
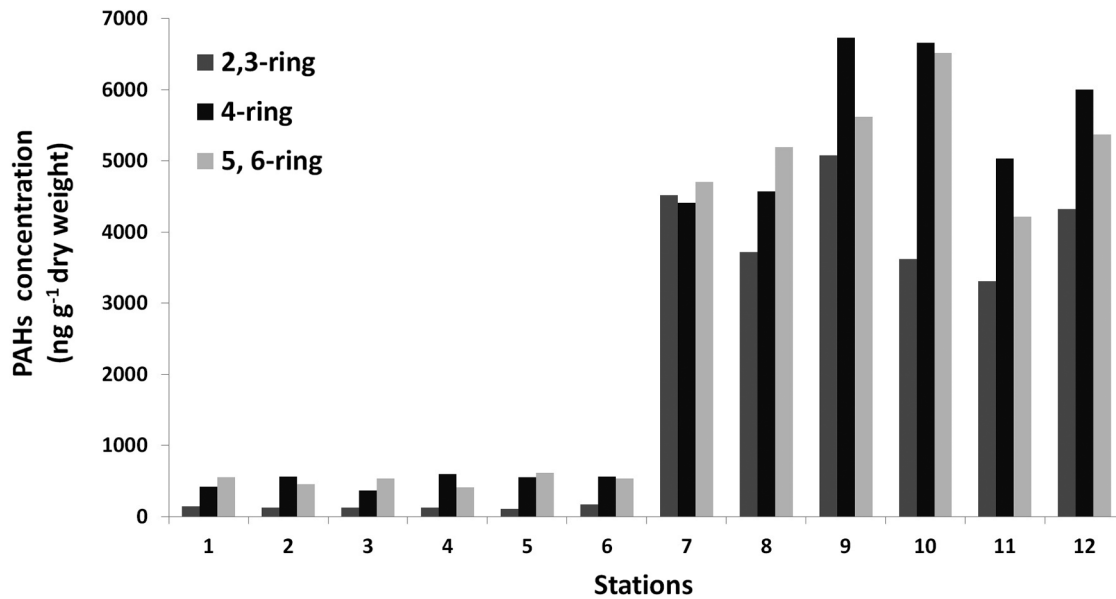

Figure 4 | PAHs composition based on benzene ring in sediment samples of 12 stations from Asaluyeh shore.

Depending on PAH composition and distribution patterns, different sources of PAHs in sediment samples can be identified. To distinguish sources of PAHs found in this study, a source analysis was carried out using PAHs isomeric ratios (ratios of individual PAH compounds) that have been widely used to determine various sources that contribute
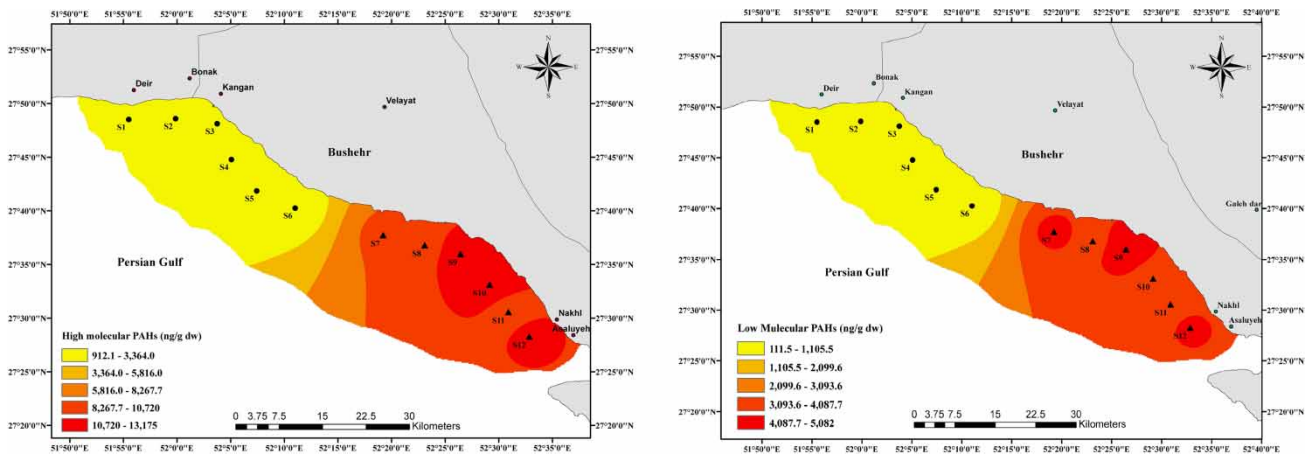
Figure 5 | PAHs composition based LPAHs and HPAHs in sediment samples of 12 stations from Asaluyeh shore.

PAHs to environmental samples (Soclo *et al.* 2000; Magi *et al.* 2002; Yunker *et al.* 2002; Fang *et al.* 2007; Jiang *et al.* 2009). The predominance of PAHs with low molecular weight (2- and 3-ring) have been linked to petrogenic sources (petroleum products), whereas PAHs with high molecular weight (4- to 6-ring) have a predominantly pyrogenic source (combustion process). Generally, a ratio of ΣLPAHs/ΣHPAHs < 1 indicates a pollution of pyrolytic (pyrogenic) origin and >1 suggests a pollution of petrogenic sources (Magi *et al.* 2002; De Luca *et al.* 2005). According to this classification, ΣLPAHs/ΣHPAHs ratios in all Asaluyeh stations were <1, showing PAHs pollution originated from combustion processes (pyrogenic sources).

Additionally, other isomeric ratios have been developed for evaluating possible PAHs sources in sediment: (a) FLU/PY or, alternatively, FLU/(FLU + PY) (Guinan *et al.* 2001; Magi *et al.* 2002); (b) PH/AN or, alternatively, AN/(PH + AN) ratio (Baumard *et al.* 1998; Soclo *et al.* 2000; Magi *et al.* 2002; Li *et al.* 2006; Qiao *et al.* 2006); (c) IP/BP (Yunker *et al.* 2002; Katsoyiannis *et al.* 2007).

The FLU/PY and FLU/(FLU + PY) ratios are helpful indicators in assessing the contribution of PAHs in sediment contamination. FLU/(FLU + PY) ratio <0.4 suggests petroleum sources, ratio >0.5 is attributed to the combustion process, whereas ratios between 0.4 and 0.5 are known to be from petroleum combustion sources (mixed sources). As shown in Figure 6, in the current study, the ratios of FLU/(FLU + PY) at nine stations (1, 3, 4, 5, 6, 7, 9, 11 and 12) were higher than 0.5, indicating that pyrogenic sources played a major role in sediment pollution. The other stations were between 0.4 and 0.5, implying that PAHs originated from mixed sources (petroleum combustion). Baumard *et al.* (1998) reported that the source of pollution is mainly

from pyrogenic sources if the ratio of FLU/PY is higher than 1. Their findings also demonstrated that petroleum discharges could increase the PAH levels in sediments if the ratio of FLU/PY is lower than 1. In this study, regarding contamination sources of 12 sampling stations, the results of the ratio of FLU/PY were completely similar to the results of FLU/(FLU + PY) ratio (Figure 6).

The PH/AN ratio is also a useful indicator to investigate the different sources of PAHs in sediments. The PH is thermodynamically more stable than AN, and higher concentrations of PH show that the PAHs pollution mainly originate from petroleum inputs. Indeed, petrogenesis activities cause a high PH/AN ratio. According to previous research, when the PH/AN ratio is higher than 10, this indicates that sediment is mainly polluted by petroleum products, and a PH/AN ratio lower than 10 shows that PAHs in sediment originate from pyrogenic activities (Baumard *et al.* 1998; Qiao *et al.* 2006). As shown in Table 3, the PH/AN ratio and AN/(PH + AN) ratio, at most stations, were lower than 10 and higher than 0.1, respectively. This means that the major source of PAHs was from combustion processes. In stations 4 and 10, the ratio of PH/AN and AN/(PH + AN) were higher than 10 and less than 0.1, respectively, showing petrogenic activities (Figure 6).

IP/BP ratio is another PAH isomeric ratio used to identify PAHs sources in sediment (Yunker *et al.* 2002; Brändli *et al.* 2007). When the ratio of IP/BP is lower than 0.2, sources are related to petrogenic inputs, and if higher than 0.5, sources are related to combustion processes, and ratios between 0.2 and 0.5 correspond to petroleum combustion. In this study, the IP/BP ratios at most stations were higher than 0.5 except in stations 2 and 6 which were between 0.2 and 0.5. Therefore, according to this isometric

Table 4 | ΣPAHs concentrations (ng/g dw) in sediments at different stations around the world (the pollution levels are assigned as low: 0–100 ng/g dw, moderate: 100–1,000 ng/g dw, high: 1,000–5,000 ng/g dw, very high: >5,000 ng/g dw (Baumard *et al.* 1998)

| Area	n[a]	ΣPAHs (ng/g dw)	Level of pollution	Literature
Asaluyeh shores, Iran	16	1,053–17,439	High to very high	Current study
Kaohsiung Harbor, Taiwan	17	34–16,700	Low to very high	Chen *et al.* (2013)
Kaohsiung Harbor, Taiwan	17	472–16,207	Moderate to very high	Chen & Chen (2011)
Pearl River Delta, China	15	52.7–717	Low to moderate	Wang *et al.* (2010)
Daya Bay, China	16	42.5–158.2	Low	Yan *et al.* (2009)
Yangtze Estuary, China	17	107–633	Moderate	Liu *et al.* (2008)
Gemlik Bay, Turkey	14	50.8–13,482	Low to very high	Ünlü & Alpar (2006)
Commercial ports from Spain	12	260–66,710	Moderate to very high	Casado-Martinez *et al.* (2006)
Norwegian Harbor, Norway	16	2,000–76,000	High to very high	Oen *et al.* (2006)
Genoa-Voltri Harbor, Italy	16	4,500–20,800	High to very high	Salvo *et al.* (2005)
Olbia Harbor, Italy	16	160–770	Moderate	De Luca *et al.* (2005)
Western Harbor, Alexandria, Egypt	20	8–131,150	Low to very high	Notar *et al.* (2001)
Hsin-ta Harbor, Taiwan	30	1,156–3,382	High	Fang *et al.* (2003)
Santander Bay, Northern	16	20–25,800	Low to very high	Viguri *et al.* (2002)
Boston Harbor, USA	16	7,300–358,000	Very high	Wang *et al.* (2001)
Izmit Bay, Turkey	17	2,500–25,000	High to very high	Tolun *et al.* (2001)
Taranto Gulf, Italy	8	335–5193	Moderate to very high	Storelli & Marcotrigiano (2000)
Baltimore Harbor, USA	21	2,944–29,590	High to very high	Pereira *et al.* (1999)
Incheon Harbor, Korea	23	12–1,400	Low to moderate	Kim *et al.* (1999)
Lazaret Bay, France	26	13,000	Very high	Baumard *et al.* (1998)
Ajaccio Harbor, Corsica	26	20,140	Very high	Baumard *et al.* (1998)
Torres Harbor, Sardinia	26	920	Moderate	Baumard *et al.* (1998)
Victoria Harbor, Hong Kong	9	1,200–14,000	High to very high	Hong *et al.* (1995)
Xiamen Harbor, China	9	2,900–61,000	High to very high	Hong *et al.* (1995)
Coastal sediment, Thermaikos Gulf, Greece	16	580–930	Moderate	Kilikidis *et al.* (1994)
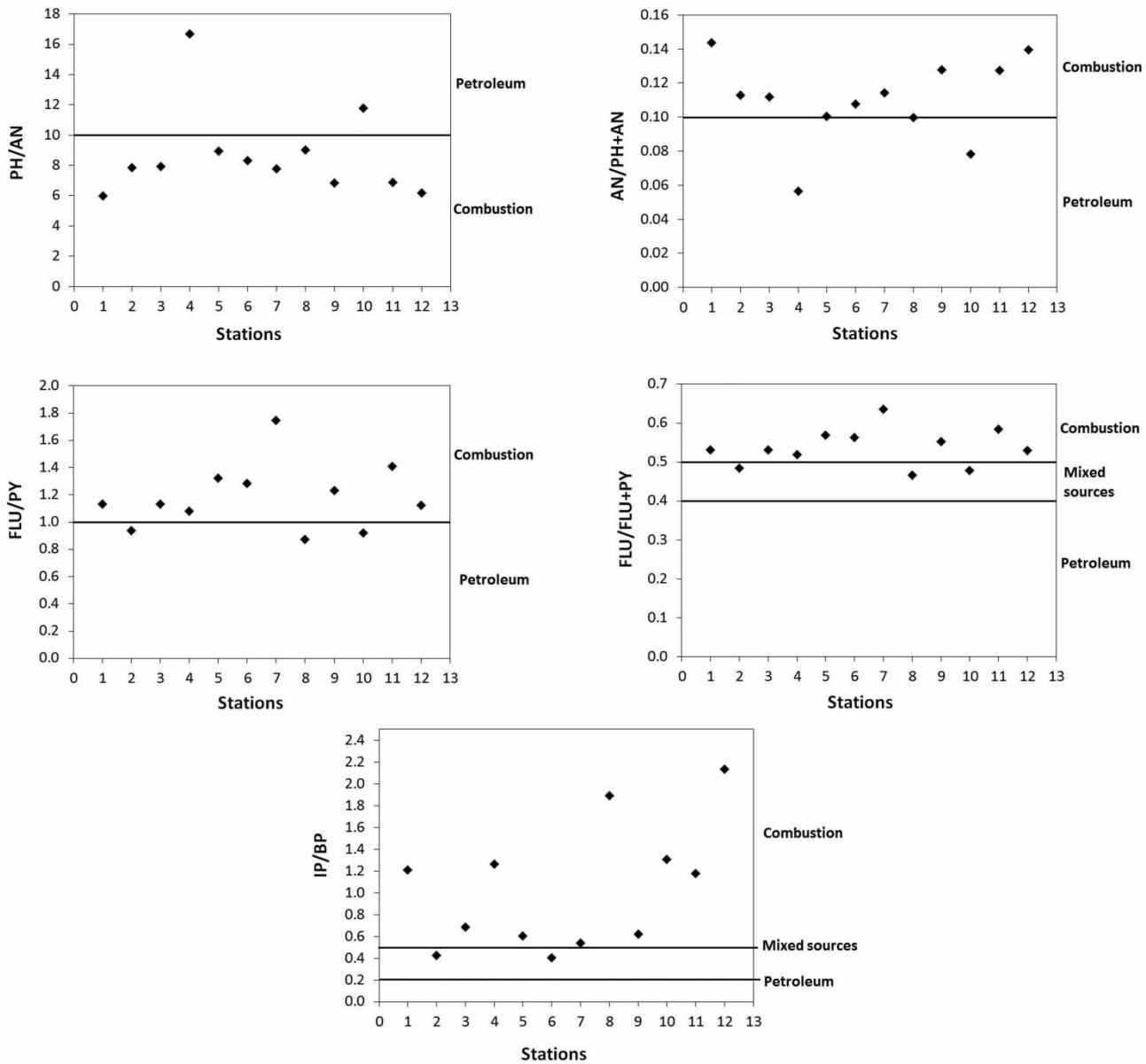
Figure 6 │ Plot of isomeric ratios PH/AN, AN/PH + AN, FLU/PY, FLU/FLU + PY and IP/BP.

ratio, pyrogenic sources were dominant (Figure 6). Based on several PAHs isomeric ratios used in this study, sediment pollution of Asaluyeh shore mainly originated from combustion processes (pyrogenic sources).

Potential human toxicity and biological effects of PAHs

Sediment carcinogenicity was evaluated in this study according to total quantity of seven potentially human carcinogenic PAHs including BaA, CH, BbF, BkF, BaP, IP, and DA (Savinov *et al.* 2003; Nadal *et al.* 2004; Qiao *et al.*

2006). As indicated in Table 3 and Figure 7, mean values of ΣCPAHs, in urban and industrial stations, were 684.1 ± 99 and 7013.7 ± 903, respectively. In addition, ΣCPAHs accounted for 43% to 67% of ΣPAHs in acquired samples of Asaluyeh sediments.

BaP is a good indicator of carcinogenic potency of sediment PAHs. Hence, the potential carcinogenicity was surveyed using the total toxic BaP equivalent (TEQ Carc) (Savinov *et al.* 2003; Nadal *et al.* 2004).

In this study, the total TEQ Carc rates of sampled sediments ranged from 172 to 2,235 ng TEQ g^{-1} dw, and the
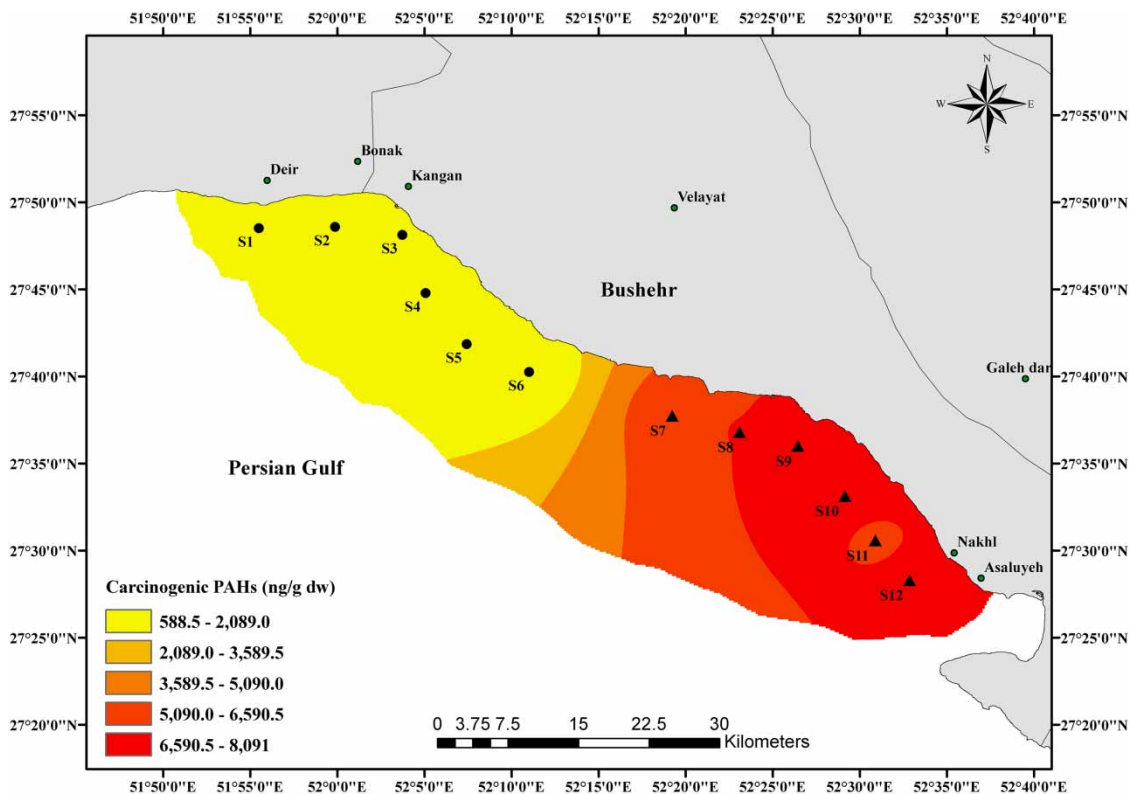
Figure 7 │ CPAHs contents in sediment samples of 12 stations from Asaluyeh shore.

average value was 998 ng TEQ g^{-1} dw. In addition, the total TEQ Carc values in industrial and urban stations averaged between 201 and 1,795 ng TEQ g^{-1} dw, respectively. Much higher pollution was seen in industrial stations compared with urban areas.

The findings of TEQ Carc in this study were consistent with sediments from Kaohsiung Harbor, Taiwan (55–1,964 ng TEQ g^{-1} dw), but higher than those reported in the Barents Sea, Russia (19–733 ng TEQ g-1 dw) and in Meiliang Bay, China (94–845 ng TEQ g-1 dw), but were lower than those reported from Naples Harbor, Italy (2–4,723 ng TEQ g-1 dw) (Chen & Chen 2011; Qiao *et al.* 2006; Sprovieri *et al.* 2007).

SQGs have been widely used for contaminated sediment assessment (Bothner *et al.* 1998; Connor *et al.* 1998; Wakeman & Themelis 2001; Birch & Taylor 2002; Jones-Lee & Lee 2005; Roach 2005). ERL and ERM are considered guidelines to help categorize the range of environmental contaminants. If concentrations are lower than ERL, this means that the biological effects are scarcely observed. If concentrations are equal to or greater than the ERL but below the ERM, it shows that a negative biological effect would occur occasionally. Concentrations at or above the

ERM indicate that a negative biological effect would frequently occur (Long *et al.* 1995).

SQGs (ERM and ERL values) in comparison with quantified PAHs in sediments of Asaluyeh are shown in Tables 2 and 3. ΣPAHs concentrations in sediment of urban areas (stations 1–6) were below the ERL, but all the industrial stations had ΣPAHs concentrations above the ERL and lower than ERM. Regarding ΣLPAHs, all of the urban sediment samples were below the ERL, whereas all of the industrial samples exceeded ERM. ΣHPAHs were below the ERL in urban samples, between ERL and ERM in stations 7 and 11, but exceeded ERM in stations 8–10 and 12 which implies that biological effects could occur frequently. Additionally, some individual PAHs exceeded ERM in industrial sediments including NA at station 12, ACE at stations 7 and 11, FL at stations 9 and 10, PH at stations 7 and 9, BaA at station 9 and BaP at station 10. In general, these results show that adverse ecotoxicological risk effects rarely occur in urban areas, occasionally occur in industrial areas, and frequently occur in some industrial stations. Industrial areas, due to various anthropogenic inputs, represent higher potential negative biological effects compared with urban areas.
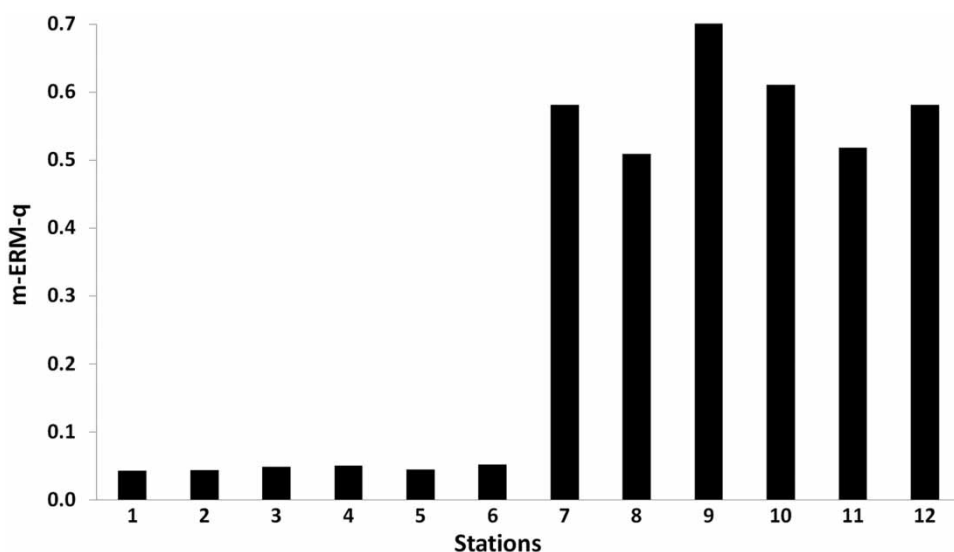
Figure 8 | The m- ERM-q values of sediment samples in 12 stations from Asaluyeh shore.

The m-ERM-q of ΣPAHs in 12 sampling stations is shown in Table 3 and Figure 8. The m-ERM-q of ΣPAHs rates in sediment from 12 stations ranged from 0.043 to 0.740 with a mean value of 0.319 ± 0.28. Stations 1–6 (urban areas) are specified as a low group (11% probability of toxicity), and stations 7–12 (industrial areas) are specified as a medium-high group (46% probability of toxicity).

However, even though the SQGs sets can somewhat predict the possible ecological toxicity of chemical contaminants, these sets do not consider chemical bioavailability and are not based on experiments (Long *et al.* 2000). Additionally, since data from all chemical contaminates, and possible negative effects are not available, SQGs cannot represent a comprehensive picture of sediments quality. Nevertheless, the value range gives for quick information for the identification of sediment quality and the ecological and biological toxicity (Long *et al.* 1998, 2000). Therefore, this measure is useful for an initial ecological risk assessment. Due to negative carcinogenic, teratogenic and environmental effects caused by the presence of this pollutant in our water systems, it is essential to continue conducting local biological toxicity experiments in order to protect against a pollution problem reaching a stage in which the livelihood of local residents and health of the local environment can no longer be sustained.

In this study, only PAH pollutants were evaluated in the northern part of the Persian Gulf, whereas there are several concerning pollutants such as polychlorinated biphenyls and dioxin that could increase along the Persian Gulf in Asaluyeh shores due to industrial activities. Therefore, the present study presents primary data on the assessment of sediment quality in Asaluyeh shores. In the near future, we hope to perform more projects to obtain comprehensive data on various possible pollutants in the sediments and seawaters along the Persian Gulf in this area.

CONCLUSION

This research provides important information on PAH levels in surface sediments of the Asaluyeh shore. A positive correlation was found between organic matter content and PAHs concentrations in sediments samples. The results show that the surface sediment from Asaluyeh shore is high to very highly contamination and PAH levels in industrial stations were much higher than in urban stations. Based on several PAHs isomeric ratios, sediment pollution mainly originated from combustion processes (pyrogenic sources). ΣPAHs concentrations in sediments from urban areas were below the ERL, but all the industrial samples had ΣPAHs concentrations between ERL and ERM. Additionally, ΣHPAHs and some individual PAHs in some industrial stations exceeded ERM, indicating that adverse ecotoxicological risk effects could frequently occur. The findings of our study suggest that industrial activities play important roles in increasing PAH pollution in sediments of Asaluyeh shore.

ACKNOWLEDGEMENTS

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