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Distribution, source finding, and ecological hazard of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in coastal surface sediments of South Pars industrial region (Iran)

Alireza Ghadrshenas Islamic Azad University Bushehr Branch Tayebeh Tabatabaie Islamic Azad University Bushehr Branch Fazel Amiri (∑ famiri@iaubushehr.ac.ir)

Department of Environment and Natural Resources https://orcid.org/0000-0003-0941-9679

Abdul Rahim Pazira

Department of Environment, Branch Bushehr, Islamic Azad University

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Distribution, source finding, and ecological hazard of polycyclic aromatic
Pars industrial region (Iran)
Alireza Ghadrshenas ¹ , Tayebeh Tabatabaie ² , Fazel Amiri ^{3*} , Abdul Rahim Pazira ⁴
¹ PhD Student, Department of Environment, Branch Bushehr, Islamic Azad University, Bushehr, Iran. Email: <i>ghadrshenas1346@gmail.com</i>
² Department of Environment, Branch Bushehr, Islamic Azad University, Bushehr, Iran. Email: <i>tabatabaie@iaubushehr.ac.ir</i> .
³ Department of Environment, Branch Bushehr, Islamic Azad University, Bushehr, Iran. Corresponding author e-mail address: <i>famiri@iaubushehr.ac.ir</i> ; Tel: +989177798200, Fax: (+98)-7733337503
⁴ Department of Environment, Branch Bushehr, Islamic Azad University, Bushehr, Iran. Email: <i>abpazira@gmail.com</i>
Research Highlights
- The first ecologic risk assessment of PCBs in south Pars coastal sediment.
- The first source finding of PCBs in south Pars coastal sediment.
- PAHs ecologic risk assessment and source finding.
- Increases in pollutants were found in the vicinity of industrial units.
- Increases in carcinogenic compounds in the vicinity of industrial units.
- Spatial distribution of PCB and PAH compounds in the South Pars region.

Distribution, source finding, and ecological hazard of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in coastal surface sediments of South Pars industrial region (Iran)

35

36 Abstract

37 The South Pars Industrial Zone is one of the most important regions in Iran due to the presence of gas, petrochemical, and 38 related industries which is known as Iran's energy capital. In this study, the effects of pollution made by polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) on coastal sediments were investigated. Ten stations in 39 40 different places such as vicinities of industries exit flow, ports, shipping terminals, export tanks, beaches and their surface 41 sediments were selected and sampled for analysis in summer and winter in 2019. The samples were tested using the gas 42 chromatography-mass spectrometry (GC-MS) analyzer. Concentrations of $\sum PAH$ and $\sum PCB$ were measured in the range of 26.50–306.45 ng, g^{-1} dw (dry weight) and BDL (below the detection limit) –59.70 ng, g^{-1} dw, respectively. There was a 43 44 significant increase near the outputs of refineries, petrochemicals, and the shipping industry. The ecological risks were 45 reported "low" in all stations for PAH components, except for one station that recorded moderate levels of Acenaphtlen 46 (Ace) and Fluorene (Flu) in the summer. The ecological risks related to PCB components were found to be in low-moderate 47 levels. Three sources were suggested for PAHs: petrogenic (31%), fossil fuel combustion (51%), and biomass/coal 48 combustion (18%). Power plants and wastewater treatment units (34%) and electrical waste disposal sites (66%) were 49 predicted as the main sources of PCBs. It is necessary to prepare and implement a long-term monitoring plan for all outlets 50 to the sea such as electrical waste.

51

52 Keywords: Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Ecologic Risk
53 Assessment, South Pars Coastal Sediment, Source Finding and Spatial Distribution

54

55 Introduction

About 600 million people worldwide are living within 10 m from the sea so their health and life depend on marine sources
and is endangered by pollution(Loiseau et al. 2021). Eighty percent of marine pollution comes from land-based activities,

58 (Landrigan et al. 2020) such as oil, gas, petrochemical industries, energy production, transfer units, industrial waste storage

59 sites, storage tanks, facilities, and export terminals (Kunili et al. 2021Nozar et al. 2014). The most important pollutants in

60 the above activities are the persistent organic pollutants (POPs) (Benson et al. 2020).

61 Coastal sediment pollution caused by PAHs and PCBs is the most harmful marine pollution due to their physical and 62 chemical properties such as hydrophobicity, carcinogenicity, lipophilicity, and stability in the marine environment. These 63 compounds also have harmful effects on human health such as embryonic abnormalities and fetal stillbirth; therefore, they 64 can be the main cause of many cancerous diseases due to their concentrations. (Löf et al. 2016) (Aghadadashi et al. 65 2019Park et al. 2020) (Girones et al. 2021Guo et al. 2019). The US Environmental Protection Agency (US-EPA) released a 66 list containing 16 combinations of PAHs as environmental pollutants including seven combinations known to cause cancer 67 in humans called carcinogenic polycyclic aromatic hydrocarbons (CPAHs) (Farrington. 2020).

- 68 The United Nations Environment Program (UNEP) estimated that 83% of previously produced PCBs still exist in the
- 69 environment, which is why they need to be treated and removed properly (EPA. Mahmoudi et al. 2020). Contamination
- 70 with PCBs has been reported in the samples taken from water and sediments worldwide. (Sakizadeh. 2020) In this regard,
- 71 some studies conducted in recent years are reviewed here.
- 72 The levels of PAHs and PCBs in the northern vicinity of Persian gulf reported 55.3-1231.6,2-5-462ng.g⁻¹dw,
- respectively (Nozar et al. 2014). The total PAHs in Qatar marine environment was observed to be 3.15-14.35 ng. g⁻¹ dw.
- 74 (Hassan et al. 2018). The levels of PAHs and PCBs in the Sea of Marmara were analyzed and reported to be lower than the
- allowable limits (Kunili et al. 2021).
- According to sediment quality guidelines (SQGs), the potential ecological risks of PAHs in sediments along the Yangtze river Estuary Deepwater Channel are at low to medium levels (X. Liu et al. 2020). Also, PCB contamination was studied globally within the last three decades, which the most polluted area with numerous heavy factories and residential was
- 79 reported to be the Italian Ionian Sea.
- Pars gas field is located 105 km away from the nearest coast in Iran in the north of Persian Gulf. This area has led to the
 development of oil refineries and other industrial complexes in the region(Samadi Kuchaksaraei et al. 2021). The
 development of industries have led to population growth and resulted in an increase in the number of transportation services
 on these beaches.
- Assaluyeh city, the most important industrial city in Iran, is constrained by the Persian Gulf from the south and the mountains from the north. Large and polluting industries such as petrochemical complexes, gas refineries, power plants, storage tanks, and export wharves near the urban fabric (Danesh et al. 2021), have the potential to produce and emit PAHs
- and PCBs (Benson et al. 2020Dumanoglu et al. 2017Sari et al. 2020). In the years 2016.17 Arfaeinia et al. and Hossein
 Khezri et al. reported the levels of PAHs and PCBs in the south pars industrial especial zone coastal area as 54.44-
- 292.72ng. g⁻¹dw,312-10965pg. g⁻¹dw respectively (Arfaeinia et al. 2017Hoseyn Khezri et al. 2018).
- 90 Recently, most industrial units such as refineries, power plants, petrochemical complexes, and new export facilities have
- 91 reached full potential in operation, making it essential to upgrade the pollution situation and increase the effectiveness of 92 remedial measures.
- 93 To the best knowledge of the authors, there has not been a similar study conducted on the ecological hazards and source
- 94 finding of PCBs in the coasts of the South Pars Industrial Zone, the results of this study can be a sufficient guide for further 95 studies to reduce the risk of possible damage to the environment.
- 96 The main goals of the present study are first to provide spatial distribution maps of PAHs and PCBs in coastal sediments,97 secondly to determine the origin while assessing the ecological risk of PAHs and PCBs.
- 98

99 Material and Method

Study area

101 The south Pars Industrial Zone is located on the shores of Persian Gulf, 300 km on the east of Bushehr and 570 km on the 102 west of Bandar Abbas (which are two important ports in Iran). There are a combination of light and heavy industries such as 10 gas refining complexes, 7 petrochemical complexes, power generation units, and storage tanks, export facilities in the

- 104 vicinity of residential and commercial areas of Assaluyeh city. The geographical coordinates of the mentioned region are
- 105 27.53438 to 27.41403 N and 52.25648 to 52.67028 N with an approximate area of 521.5 square kilometers. The climate of
- the region is excruciating hot and humid (Figure 1) (Mahmoudi et al. 2020).





109

110 - Sampling method and collection of samples

According to the purpose of the study, to investigate the role of industrial outputs in marine pollution, sampling stations was selected by a suitable systematic method. (Batley et al. 2016) Ten stations were considered along the sea line of the south pars industrial regions adjacent to the industrial zone, ports, discharge points, residential areas, and one beach site far from the potential contamination sources as a control station (Fig. 1). Each station was sampled twice in summer and winter 2019 (winter and summer) (Hoseyn Khezri et al. 2018). Surface sediments were sampled (Odabasi et al. 2017). Sampling points were positioned by the Global Positioning System (GPS).

Samples were collected by Van Veen Grub sampler with an area of 250 cm2 (made of stainless steel, with approximate dimensions of $55 \times 30 \times 22$ cm and mass 5 kg). The water depths of the sampling sites were in the range of 10 to 32 meters.

119 Approximately 350 grams of uniform sediment was stored in aluminum containers and sent to the laboratory in an icebox.

- 120 The physical and chemical parameters of seawater such as PH, temperature, and salinity were also measured at each
- 121 station(Odabasi et al. 2017).
- 122 Samples preparation
- 123 Samples after freeze-drying kept laboratory until the test at -20 °C (Nozar et al. 2014)
- 124
- 125 PCBs Extraction

The frozen samples were crushed and passed through a sieve with a mesh size of 250 μm. Then, 20 g of the sample was
weighed and transferred without hands using aluminum foil fingers and pliers. Moreover, 1 ml of a PCB 198 and PCB 29

solution with a concentration of20 ng/ml was added as an internal standard. Extraction was performed with 250 ml of hexane/dichloromethane solution (50:50 ratios) and many boiling stones for 8 hours. To prepare the standard peak, 1 ml of internal standard solution was added, then Soxhlet operation was performed without any samples. The copper powder was used to remove free sulfur and mercaptans. (Benson et al. 2020).

132 - PAHs Extraction

The frozen sediment samples were crushed and passed through a sieve with a mesh size of 250 μ m Then 15 g of the samples were weighed and poured into the thimble, then extracted with a 50: 50 hexane-dichloromethane solution in Soxhlet apparatus, the internal standard was added to the sample to determine the yield. The internal standard is 50 microliters of a mixture containing 20 ng / μ l of N-C19 D40 and N-C32 D66 solution for the first fraction and about 20 ng / μ l of hexamethyl benzene, cadalene, and naphthalene D8 for the second fraction. Extraction in Soxhlet was done with 250 ml of hexane/dichloromethane mixture. The copper powder was used to remove free sulfur and mercaptans (Nozar et al. 2014).

139 - Instrumental Analysis

The samples were injected with an auto sampler to a GC/MS Agilent-7890 B, mass detector 5977, a MSD with a DB-5MS column type and chromatogram to obtain the mass spectrum. The results were compared with a calibration reference standard. The temperature program for PAHs was chosen as follows: initially, in 2 minutes it reached 160 °C and then reached the temperatures of 200, 290 and, 300 °C in 3 steps with slopes of 12, 3, and 10 °C. For PCB, the temperature reached 150 °C. Then in 3 steps, with a slope that reached 12.3 and 20 degrees Celsius to 210, 270, and 280 degrees Celsius in a minute.

PAHs and PCBs congeners: all samples were analyzed for 41 PCBs and 195 16PAHs (Nisbet et al. 1992) which are
abbreviated in Table 1. The amount of organic matter (OM) was determined by weight method via heating to 600 °C for 4 h

148 (W. Wang et al. 2011).

149 Table 1. PAH components/abbreviations

Compound	Abbreviation	Compound	Abbreviation
Benzo[a]pyrene	BaP	Acenaphthene	Ace
Benzo[a]anthracene	B(a)A	Acenaphthylene	Acy
Benzo[b]fluoranthene	B(b)F	Fluranthene	Flt
Benzo[k]fluoranthene	B(k)F	Fluorene	Flu
Indeno[123-c,d]pyrene	IND	Naphthalene	Nap
Anthracene	Ant	Phenanthrene	Phe
Benzo[g,h,i]peryIene	B(ghi)P	Dibenzo(a,h)anthracene	DBA
Chrysene	Cry	pyrene	Pyr

150

151 - QA/QC

To control the quality and ensure the reliability of results, the tests were conducted by the standards of the Iran's Department of Environment (Moghadam et al. 2018) valid articles and using devices with a valid calibration certificate. All sampling and testing equipment were washed with water and purified water, respectively. A solution with specific concentrations was prepared for PAHs and PCBs and was added to each sample and control sample to calculate the

- 156 recovery efficiency before extraction. Recovery efficiencies for PCBs and PAHs were 85.4% 107.5% and 75.4% -
- 157 115.2%, respectively. Hence, the data were acceptable and did not need to be modified
- We analyzed the data in case of the accuracy of prepared materials, a blank sample was prepared and the results below thedetection limit were read (LOD).
- 160 Standard PCB and PAH solutions were used to construct GC/MS calibration curves with five calibration points at
- 161 concentrations of 10, 50, 100, 250, and 500 ng/ml. A linear response (r2 > 0.999) was observed by the GC-MS. The method
- detection limits (MDL in terms of ng/g) for PAHs and PCBs were calculated 0.3 and 0.15 ng/g respectively.
- 163

164 - Sources finding

One of the most important classifications for PAH to obtain the source of contamination is based on the number of aromatic
 rings and their molecular weight (Ghosh et al. 2021). Regarding PCB congeners, it is based on the number of chlorine. (Lu
 et al. 2021)

- General sources for the release of PCBs congeners, such as emissions of combustion, incineration of plastic waste, leaks from sites containing PCBs compounds, coal and related waste, which are transported by air and water (Dumanoglu et al. 2017). The composition of PCBs is divided into homologs based on the number of chlorine (di-Teri-tetra-Penta –Hexa-Hepta-Octa). The source of emission is also different depending on the homolog.
- 172 Low chlorine originates from the used equipment, electrical waste and productions of unintentional products (U-PCB). The 173 sources are paint additives and building materials which are mostly released inadvertently. U-PCBs are usually the primary 174 sources of decomposition and adsorption of lightweight PCBs, which include combustion sources, process industries, power 175 plants, and incinerators.

176 - EPA's Unmix

The US EPA-UNMIX software was used to model the conditions, predict the sources of PAHs and PCBs pollution production (share detection). (Y. Wang et al. 2016). This software is based on the using share modeling and provides appropriate profiles using mathematical matrices. In principle, the model follows and applies the following equation, where xij is the concentration of specie i in sample j, f_{ik} is the concentration of specie at sources k, and G_{kj} = the share of source k in sample j (Cao et al. 2020).

182
$$X_{ij\equiv} \sum_{i} f_{ik} G_{kj}$$
 (1)

The advanced release modeling analysis using EPA UNMIX6 software was implemented to accurately identify the sources of production and release of PAHs and the share of each source, along with forecasting. After performing all components, the software was run by feeding the laboratory results and introducing three sources with a suitable signal-to-noise index (more than 1.5). The report of the model's certainty was appropriate. For more information, refer to the EPA UNMIX 6 fundamentals and user guide (EPA. 2007).

- 188
- 189

190 - Diagnostic indexes

191 The sources of PAH were detected using diagnostic indexes and EPA's Unmix software. These indicators are related to the 192 surrounding producer resources. Compounds with lighter molecular weights are the result of burning at low temperatures, 193 such as wood-burning, and those with heavier molecular weights result from burning at higher temperatures (Manoli et al. 194 2004). The diagnosis indicators of the PAH, which were used in this study, are shown in table 2(Benson et al. 2020Sari et al. 2020).

197	Origin of production	Value	Indicators Index (II)	Ref.
198	Petrogenic	II< 0.1	A	(Lorenzi et al.
199	Pyrogenic	II> 0.1	Ant. / (Ant+Phe.)	2011)
200	Petrogenic Fossil fuel			
201	combustion	II< 0.4		
202	Grass, wood, coal	< 0.5 II 0.4 <	Flt/(Flt +Pyr)	(Franco et al. 2017)
203	Biomass/coal combustion	II> 0.5		
204	Detrogenie	< 0.2 H		
205	Combustion	< 0.2.11 II> 0.35	Bap/(BaP+Chr)	(J. Liu et al. 2019)
206				
207	Pyrogenic	II< 1 II> 1	LMWPAH /HMWPAH	(Tucca et al. 2020)
208				

196 Table 2. Relative indexes used to find the origin of PAHs

209 In general, sediments are usually the destination of cyclic aromatic hydrocarbon compounds poured into the sea (Duran et 210 al. 2016). Two PAH diagnostics indices used in similar studies were used in the present study. An ant./(Ant. + Phe.) The 211 ratio lower than 0.1 indicates the production of PAH by petroleum (crude oil and its derivatives). When this index is higher 212 than 0.1, the petrogenic source is the main role in the production of compounds of the PAH is. Based on the ratios 213 mentioned in 20% of the stations in the region, Crude oil compounds were the predominant source. The reason for this is the 214 proximity of the above stations to the export tanks of oil derivatives and fishing boats, leaks, and deliberate leaks into the 215 sea. Flt/ (Flt +Pyr) were used as the second index, and a result less than 0.4 indicates the main role of petrogenic fossil fuel 216 combustion, a result in the range of 0.4-0.5 indicates the grass, wood, and coal as the main factor of production, and a value 217 greater than 0.5 represents the predominant source of biomass/coal combustion (Cao et al. 2020).

218 - Ecotoxicological Assessment

Considering the effects of PCBs and PAHs compounds on ecological sediments and their destructive role in the health of living organisms and its resulting hazards, sediment hazards in the marine environment were assessed using the information, risks, and complications of the Sediment Quality Guide (SQG) (Y. Li et al. 2017). The low impact range (ERL) and the moderate range (ERM) indicate probabilities of biological complications less than 10% and more than 50%, respectively 223 (Long et al. 1995). PAH densities below ERL, between ERL and ERM, and above ERM indicate that destructive biological

effects occur in the order of infrequently (low), occasional (moderate), and often (high) (Cao et al. 2020Y. Li et al. 2017).

225 - Statistical Analysis

226 Statistical analysis was performed by using the SPSS software, Version 22 of IBM product, copyright of 2018. In this study,

Shapiro-Wilk, Kolmogorov-Smirnov normality tests, ANOVA analysis of variance, and t-test were used. The significance
level for all results considered 0.05 (Umasangaji et al. 2020).

229 Results and discussion

230 - The density of PAHs and PCBs

The results of the density of PCBs and PAHs by the components/congeners are shown in Tables 2 and 3. PAHs were present (summer and winter) in all stations and their ranges were 26.5-306.5 and 97-210 ng. g^{-1} dw, respectively. PCBs were present in all stations in winter; stations no.1, 4, 5, and 6,8,10 in summer with the concentration range of BDL-59.7, BDL-54.4ng. g^{-1} dw, respectively. As shown in the spatial distribution of pollutants maps (Figs.4a, b), the highest concentrations of PAHs and PCBs were related to stations number 6 and 3, respectively; these two stations are close to the effluent of industrial complexes.

The average concentration of PAHs has decreased compared to the previous study in the region conducted in 2016. The maximum values increased significantly, which indicates the creation of pollution distribution points (Hoseyn Khezri et al. 2018). Concentrations of PCB congeners showed higher concentrations than studies done in the study zone and northern Persian Gulf(Arfaeinia et al. 2017) (Nozar et al. 2014). The highest concentrations of carcinogenic PAHs were reported from stations 10 (local boat pier), 9, and 6 (effluent of refineries and the port), 4 (tank repair pier), and 5 (shipping port) with percentages of 21, 15, 13, 13, and 11%, respectively.

The results showed that low molecular weight PAH compounds were predominant in 75% and medium molecular weight compounds in 25% of the study area. It was reported that Phenanthrene, Pyrene, Naphthalene, and Acenaphthene compounds have the highest concentrations at the stations, PCB18, PCB44, PCB105 were the most dominant congeners in the all stations, respectively.

As shown in Figure 5 the highest amounts of LMW-PAH, HMW-PAH compounds were observed in station number 6 (Refineries effluent and port) and station 10 (Local boat pier) 155 ng. g^{-1} dw 26.83ng. g^{-1} dw respectively. The highest amount (43.57 ng. g^{-1} dw) of low chlorine PCB congeners DI-PCB was observed in station 3 (effluent of industrial complexes) and more chlorinated PCB congeners (Penta-PCB, Hexa-PCB, and hepa-PCB) were measured at 3.45, 10.67, and 5.1 ng. g^{-1} dw at station 9, 4, and 1, respectively.

- 252
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- 255

256 Table 3. Concentrations of PCBs according to the season $(ng. g^{-1}dw)$

PCBs								
Winter			Summer					
Component	Range	Mean	Median	SD	Range	Mean	Median	SD
PCB 18	ND- 43.57	13.48	6.91	15.06	ND- 2.00	0.30	0.00	0.64
PCB 31	ND	-	-	-	ND	-	-	-
PCB 28	ND- 1.97	0.38	0.00	0.76	ND	-	-	-
PCB 44	ND- 10.85	4.47	4.52	4.17	ND- 566.00	56.60	0.00	169.80
PCB 52	ND	-	-	-	ND- 3.00	0.80	0.00	1.25
PCB 105	ND- 3.45	2.00	1.90	0.91	ND- 14.00	1.60	0.00	4.18
PCB 141	ND	-	-	-	ND	-	-	-
PCB 149	ND	-	-	-	ND	-	-	-
PCB 138	ND- 5.09	1.47	1.86	1.51	ND	-	-	-
PCB 151	ND- 5.26	1.76	1.80	1.76	ND	-	-	-
PCB 180	ND- 5.09	1.41	0.91	1.68	ND-11.00	1.10	0.00	3.30
PCB 194	ND	-	-	-	ND	-	-	-
PCBs	5.68-54.42	24.98	20.63	15.41	ND- 579.00	60.40	1.50	172.94

258 Table 4. Concentrations of PAHs according to the seasons($ng.g^{-1}dw$)

PAHs								
	Winter			Summer				
Component	Range	Mean	Median	SD	Range	Mean	Median	SD
Naphthalene	0.34-48.14	16.07	16.07	14.13	ND	-	-	-
Biphenyl	13.50-33.78	19.51	19.51	6.05	ND	-	-	
Acenaphtylen	0.25-5.06	2.06	2.06	1.34	ND- 185.5	23.08	0.00	55.08
Acenaphtlen	2.70-30.41	9.08	9.08	10.68	ND- 7.3	1.62	0.00	2.66
Florene	5.47-7.61	6.52	6.52	0.66	ND- 35.2	4.69	0.50	10.31
Phenanthrene	19.97-41.74	29.73	29.73	6.06	ND- 8.5	4.19	4.17	2.10
Anthracene	13.32-20.58	16.58	16.58	2.02	ND- 14.0	6.88	6.45	3.60
Fluoranthene	0.23-14.20	8.96	8.96	4.57	ND- 4.4	1.87	1.55	1.22
Pyrene	1.13-61.69	26.96	26.96	16.58	ND- 17.5	5.57	2.90	5.68
Benzo(a)ant	0.82-2.30	1.60	1.60	0.44	ND- 3.9	0.60	0.00	1.27
Chrysene	ND-3.70	0.82	0.82	1.32	ND- 5.8	0.89	0.00	1.88
B(b)F	0.38-11.62	2.47	2.47	3.23	ND- 86.0	36.99	23.50	33.13
B(k)F	ND-8.54	4.39	4.39	2.61	ND- 65.8	36.44	45.75	25.21
B(a)P	0.20-26.73	7.59	7.59	7.41	ND- 12.5	5.79	5.40	4.25
Dibenzo(a,h)Anthracene	ND	-	-	-	ND- 9.6	0.96	0.00	2.88
Benzo(g,h,i) PeryIene	.ND	-	-	-	ND- 0.9	0.09	0.00	0.28
Indeno(1,2,3cd)Pyrene	.ND	-	-	-	ND- 8.4	1.78	0.00	2.70
$\sum PAHs$	97.94-210.49	152.35	152.35	30.17	ND- 306.7	131.45	125.55	79.25



Figure 2. The spatial distribution of PAHs (GIS software output)



264 Figure 3. The spatial distribution of PCBs (GIS software output)

b



267 Figure 4. Concentrations of PAHs (a) and PCBs (b) measured in $ng.g^{-1}dw$



269 - Impacts of changes

The statistical analysis of the results by statistical software and the t-index indicated no significant changes in the results of PCBs which were obtained in the summer and winter (p = 0.05). On the other hand, the concentrations of PAHs were significantly correlated with seasonal changes (p = 0.05). In summer, the concentration increased significantly; therefore, this can refer to the Persian Gulf marine meteorological conditions.

The main cause of sediment deposition in waters, seas, and estuaries is done by currents and the dynamics of water movement (W. Li et al. 2021). In summer, the organic matter settles in the seabed, and the organic matter of the sediment reaches its maximum, which shows a significant increase compared to that of winter (Pruski et al. 2021). Due to the role of the South Pars Industrial Zone in supplying Iran's gas in winter and the need to have the units repaired in summer, the probability of pollutants entering the storage tanks and the sea in summer increases. (Kaveh Pishghadam et al. 2021Sarkheil. 2021).





Figure 5. Concentrations of PAHs and PCBs (A: summer and B: Winter) measured in ng.g⁻¹dw

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285 - Source finding

286 <u>PAHs</u>

According to the results as shown in Fig6, 70% of the stations were the predominant source of fossil fuel combustion and vehicle combustion (the activity of commercial and fishing boats is seen in the above stations), and 30% of the stations are the predominant source of biomass/coal combustion, which can be caused by proximity to the output of industrial complexes and wastewater treatment plants. In the present study, the first release factor of PAH compounds was vehicles and subsequent biomass production.

292



293

Figure 6. The diagnostic ratio ant/(ant+phe) vs. Flt/(Flt+Pyr). Flt, Pyr, Ant, and Phe symbolize Fluranthene, pyrene,
 Anthracene, and Phenanthrene, respectively.

296

297 Three sources according to the UNMIX report were identified. Examinations of the conditions of the study area were as298 follows.

299 1- Petrogenic / natural (crude oil and its derivatives ((discharge to the sea)) and discharge of port effluent and storage
 300 tanks).

301 2- Fossil fuel combustion (vehicles and traffic)

302 3- Biomass combustion sources / incomplete combustion and discharge of wastewater treatment units of gas and

petrochemical industries. The charts show the results of modeling (Figs.7, 8).



305 Figure 7. Prediction and measurement indicate the appropriateness of matching the actual and predicted values by the 306 model

304

308 <u>PCBs</u>

Two main sources were predicted for PCBs. In the first source High-chlorine compounds (PCB105, PCB131, PCB151, and
PCB180) were found to be dominant with 68.1%. These congeners were used in a high percentage of commercial
compounds PCB1254 and PCB1260, which had various applications such as electric converters, gas distribution turbines,
hydraulic fluids, adhesives, rubbers, heat transfer systems, wax diluents, and carbon-free papers (Information. 2021). This
source can be considered as industrial units such as power plants and industrial wastewater treatment units of industrial
complexes and refineries.
In source 2, low-chlorine compounds (PCB 18, PCB28, and PCB44) were in the majority with 93.4%. These compounds

316 make up a high percentage of arcolor1016 and mostly were used as capacitors and electrical insulators. This source can be

317 considered as electrical waste disposal sites.



318 Figure 8. The percentage of production sources of PAHs and PCBs in the study area

319 - Ecological risk evaluation

The results of ecological risk of all stations except Station 7 were assessed as "low" (Table 3). As the station was located near the outlets of storage tanks, ports, refineries and other industries, this result shows the role of industries in coastal pollution.

323

Table 5. PAH densities (mg/kg) of PA, Hs, ERL, and ERM (Burton. 2002)

РАНс	EDI	ERM	Current study		
I AIIS	EKL		Min.	Max.	
Naphthalene	0.16	2.10	0	0.0073	
Acenaphthylene	0.04	0.64	0	0.1855	
Acenaphthene	0.02	0.50	0	0.0352	
Fluorene	0.02	0.54	0	0.0085	
Phenanthrene	0.24	1.50	0	0.014	
Anthracene	0.085	1.10	0	0.0044	
Fluoranthene	0.60	5.10	0	0.0175	
Pyrene	0.66	2.50	0	0.0039	
Benzo(a)anthracene	0.26	1.60	0	0.0058	
Chrysene	0.38	2.80	0	0.086	
Benzo(b)fluoranthene	0.32	1.88	0	0.0658	
Benzo(k)fluoranthene	0.28	1.62	0	0.0125	
Benzo(a)pyrene	0.43	1.60	0	0.0096	
Dibenzo(a,h)anthracene	0.43	1.60	0.0000	0.00094	
Indeno(123-c,d)pyrene	0	0	0.0000	0.00814	
Benzo(g,h,i)perylene	0.063	0.26	0.0000	0.00094	
Σ16PAHs	4.02	44.79	0.0265	0.30645	
LMW	0.55	3.16	0	0.237	
HMW	1.70	9.60	0	0.229	
Total PCBs	0.023	0.18	0	0.0597	

ERL — Effect Range Low; ERM — Effect Range Median Long (1992), (Burton. 2002).

324 - Comparison with other studies

Comparison of the results of the present study with the reported studies (Table 6) has shown that the concentration of PCBs and PAHs, and ecological hazards are lower than in the northern part of the Persian Gulf. However, compared to the previous study conducted on the coasts of Assaluyeh, the coastal areas adjacent to the Aliaga Industrial Zone in Turkey and the coastal areas of Qatar and Bahrain are more concentrated due to the commonality of the coastal areas under study with the coasts of Qatar and Bahrain (Persian Gulf), pollution monitoring and removal is essential.

330 Table 6. Some ecological risks from world waters

Study area	Ecological risk	Component (ng·g-1dw)	Reference	
Urbanized semi-enclosed Jiaozhou Bay, China	Rarely	PAH: 37.7-290.9	(Cao et al. 2020)	
Northern Persian Gulf	The sites with amounts > ELR 10.3% and > ERM were estimated at 2.9%	PAHs: 55.3-1231.6 PCBs: 2.5-462	(Nozar et al. 2014)	
KimNguu river, Northern area of Vietnam	Low to medium risk	PAHs: 3.57 to 84.39 PCBs: 4.73 to 36.34	(Toan et al. 2020)	
Danshui River basin, Taipei, Taiwan	Relatively low	PCBs: 0.02 to 54.9 PAHs:96 to 3803	(Cheng et al. 2020)	
South pars industrial region coast	Low to moderate	PAHs:26.5-306.45 PCBs: 0-59.7	Current study	
Aliaga industrial region, Turkey	-	PAHs:35.5–49,682 PCBs:2.7–2450	(Odabasi et al. 2017)	
Pearl River Estuary China	Medium	PCBs: 4.6 to 187.4	(Tang et al. 2020)	
Volturno River, Southern Italy	The integrity is possibly at risk.	PCBs: 4.3 to 64.3	(Montuori et al. 2020)	
Lagos lagoon, Nigeria	considerable	PAHs:1.43–5.90 PCBs: BDL – 6.41	(Benson et al. 2020)	
Liaohe Estuary, China	Low	PCBs: 106.7 to 270.0 pg·g-1dw	(Zhong et al. 2020)	
Multi-industrial city of Ulsan, South Korea	-	The mean concentration of $\Sigma 16$ PAHs was 722.	(Seo et al. 2020)	
Marine sediments collected from the Kingdom of Bahrain	Low	-	(Bersuder et al. 2020)	
Qatar marine environment	Low	PAHs were in the range of 3.15–14.35	(Hassan et al. 2018)	
Persian Gulf surface sediments, Bushehr, Iran	Low	The range of total 15 PAHs in sediment was from 6.5 to 35.5 ng g-1	(Bateni. 2019)	
The Persian Gulf, five commercially important fish species from Larak coral Island, Iran	Low	PCBs in surface sediments $2.95-7.95 \text{ ng g}^{-1}\text{dw}$	(Ranjbar Jafarabadi et al. 2019)	
Pars Special Economic Energy Zone, Iran	Lower than the standard limits	PAHs in sediment was 292.72±54.44 ng/g dw	(Hoseyn Khezri et al. 2018)	
heavily industrialized area of Assaluyeh, Iran		PCBs in surface sediments : 313-14107pg g-1dw	(Arfaeinia et al. 2017)	

333 - Conclusion

Nowadays, pollution can be one of the main concerns due to the presence of stable organic compounds, such as PAHs and 334 335 PCBs in aquatic areas, especially in coastal areas. The present study demonstrated that the concentrations of PAHs and 336 PCBs increased in locations close to the outlets of refineries, other industrial complexes, and shipping industries compared 337 to other areas. However, the environmental risk was evaluated from low to medium according to the defined indicators. In 338 the report of resource analysis in places with activities such as exporting petroleum products and fishing boat routes, the 339 predominant sources of PAHs were shown to be petrogenic. The predominant sources of PCBs were power plants, 340 wastewater treatment plants, and landfills. Thus, it is necessary to prepare and implement a long-term monitoring plan for all outlets to the sea such as electrical waste. Possible leaks must be repaired and deliberate dumping of materials into the 341 342 sea must be prevented. Likewise, further studies focusing on other persistent organic pollutant classes, origins of 343 compounds, and sampling of fish and other marine organisms are required.

344

Author contribution Fazel Amiri and Tayebeh Tabatabaie: conceptualization, methodology, writing-reviewing, and
 editing. Alireza Ghadrshenas: sample preparation and chemical analysis. Abdul Rahim Pazira: writing, reviewing, and
 editing. All authors read and approved the final manuscript.

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352

353 Conflicts of 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.

356

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