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RESEARCH ARTICLE

Heavy metal and persistent organic pollutant profile of sediments from marine protected areas: the northern Persian Gulf

Maryam Ghaemi[1] · Farshid Soleimani[1,2] · Sara Gholamipour[1]

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Abstract

Marine protected areas (MPAs) are one of the policy tools to support marine biodiversity conservation and sustainable use of marine resources. The distribution, sources, and ecological risk assessment of persistent organic pollutants (POPs), including polycyclic aromatic hydrocarbon (PAHs), total petroleum hydrocarbons (TPHs), polychlorinated biphenyls (PCBs), and heavy metals (HMs) in sediments of MPAs in the northern Persian Gulf, were evaluated for the first time in this study. The Σ_{16}PAHs ranged from 4.65 to 20.86 µg/kg dry weight (dw). The molecular ratios and ring's pattern of PAHs suggested a mixed origin with a predominance of pyrogenic sources. The TPH concentration varied from 5.21 to 17.90 µg/g dw. Ecological risk assessment suggested that sediment samples in Bushehr Province's MPAs can be categorized as medium risk. The mean concentration of $\sum_{18}$PCB was 0.345–0.419 ng/g dw, and the main components correspond to PCB-77, PCB-105, PCB-81, PCB-101, and PCB-114. The mean concentration of As, Co, Cr, Ni, V, Mg, Pb, Zn, Cu, Al, and Fe varied from 4.79 to 9.69, 2–12, 39–142, 18–90, 15–58, 184–425, 7–45.9, 6–42.4, 4–20 µg/g dw, 0.75–4.12%, and 0.35–1.62%, respectively. Multivariate analysis, such as principal component analysis (PCA) and cluster analysis (CA), coupled with correlation coefficient analysis, was used to analyze the analytical data and to identify possible pollution sources. The results of this study provided the background information on the extent of POP contamination in the sediment and highlighted the need to further control pollution in MPAs.

Keywords Persistent organic pollutants · Polycyclic aromatic hydrocarbon · Polychlorinated biphenyls · Heavy metals · Marine protected area · Persian Gulf

Introduction

Marine ecosystems are a significant source of food, revenue, and recruitment. They offer a variety of other services, including coastal protection against extreme weather incidents such as storms and floods, marine biodiversity, and carbon sequestration, which are important for human welfare (Bijma et al. 2013). Marine ecosystems are under severe pressure due to various human activities and are expected to rise. These pressures can re-enforce each other, applying collective impacts on marine ecosystems and biodiversity.

The Persian Gulf (PG) is a semi-enclosed marginal sea of the Indian Ocean and, through the Strait of Hormuz, connects to the global open waters (Massoud et al. 1996). The main river inflows into the Gulf (formed by the Shatt Al Arab, Mond, Helleh, and Hendijan rivers) are placed at the northern end of the PG, mainly on the Iranian side (Reynolds 1993). The Gulf is one of the most significant marine habitats and home to rich biodiversity, including ornamental fish and edible and non-edible fish as well as marine turtles, dolphins, and sharks (Kor and Mehdinia 2020). The marine environment of the PG is one of the most physiologically stressful environments (Price 1993; Sheppard 1993). As a result of the long residence time of water in the PG (between 3 and 5 years), pollutants that entered into the Gulf receive limited dilution, thus dispersing more slowly than would happen in a more open circulating marine basin (Freije and Awadh 2009). The main environmental

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✉ Maryam Ghaemi
maryam.ghaemy@gmail.com

[1] Iranian National Institute for Oceanography and Atmospheric Science, No. 3, Etemadzadeh St., Fatemi Ave., Tehran 1411813389, Iran

[2] Tobacco and Health Research Center, Hormozgan University of Medical Sciences, Bandar Abbas, Iran

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pressures on the marine ecosystems of the PG are oil and petrochemical industry, dredging, shipping and transport, residential, industrial development, mining, fishing, tourism, agriculture, and excessive inputs of hazardous substances, including pesticides, PCBs, PAHs, TPHs, anionic surfactants, heavy metals, and micro-/nanoplastics (Sheppard et al. 1992; Fowler et al. 1993; Price 1993; Sheppard et al. 2010; Aghadadashi et al. 2019a, 2019b; de Mora et al. 2010; Keshavarzifard et al. 2018).

Marine protected areas (MPAs) are one of the policy tools to support marine biodiversity conservation and sustainable usage of our massive vulnerable ecosystems (OECD 2017). MPAs cover around 4.12% of the entire marine environment. MPAs have been defined as a section of the ocean with its overlying water and related flora and fauna which has been kept by law or other efficient ways to preserve portion or all of the surrounding environment (Kelleher 1999). Different chemical pollution is a known threatening factor for MPAs (Abessa et al. 2018). Most entered contamination into MPAs originates from terrestrial sources. MPAs located crossways shipping lines or nearby industrial and/ or port facilities, towns, and mouth of rivers experience considerable water pollution (Rodríguez-Rodríguez 2019). Recent studies have shown that the MPAs are threatened by the toxic pollutants (Moreira et al. 2021). Monitoring of the quality parameters and pollutants of water and sediments in the MPAs is essential to establish ecological baseline data and to assess trends in performance over time (OECD 2017).

Although the inventory of the existing literature shows that little information is available on the pollution conditions in the world MPAs (Huntley et al. 1995; Metwally et al. 1997; Barakat et al. 2013; Nozar et al. 2014; Zhang et al. 2015; Habibullah-Al-Mamun et al. 2019; Ranjbar Jafarabadi et al. 2019; Zahedi Dehuii et al. 2019; Uddin et al. 2021), the status of contaminant concentrations in the PG marine protected areas is still unknown. The objective of the present study was to evaluate for the first time the levels of emerging contaminants in the sediments of MPAs in the northern PG and to recognize the possible sources of these contaminants, setting a baseline for these critical areas. It is projected that these results will be used as a baseline assessment tool for the ecosystem quality and may have full implications for future conservation strategies and management plans in these zones.

Materials and methods

Study area and sampling

Sediment samples were collected from MPAs along the northern coasts of the PG (8 stations in total), including Helleh protected area (H1 and H2 stations), Nayband National Park (NB1 and NB2 stations), Mond protected area (M1 and M2 stations), and Nakhilo National Park (NL1 and NL2 stations), as a part of "The PG and Gulf of Oman Oceanographic Monitoring Program" initiated by INIOAS and Iran National Environment.

Helleh and Mond areas on the south coast of Iran were included as MPAs, and Nayband and Nakhilo areas as marine national park in order to protect and preserve these marine spaces that are representative of ecosystems and habitats under environmental policy purposes. However, these areas are influenced by the combined discharge of Mond and Helleh rivers (Pouladi et al. 2013) and different anthropogenic activities such as road construction, dam construction, agriculture, aquaculture, fishing, shipping, and oil and gas activities.

The Mond protected area with an area of 46,500 ha is located in the south of the Mond River and near the North Pars gas facilities. Aquaculture (the Mond shrimp farm harvests 3 t of shrimp per acre twice a year) and agriculture activities are the primary sources of income for the local population.

The Helleh protected area is located on the shores of the Persian Gulf with an area of 44,783 hectares, about half of which is a wetland, and its water comes from the Helleh River. This area is an essential habitat for migratory birds. Aquaculture, agriculture, and fishing activities are primary sources of livelihood for the local population.

The Nakhilo National Park, with an area of 20,000 ha, includes the uninhabited islands of Nakhilo, Tahmadon, and Umm-Algorm, which are suitable places for birds and turtles to lay their eggs, as well as the Mele-e-Gonzeh mangrove forest.

The Nayband marine national park, with a total area of 49,815 ha, includes several large marine estuaries, mangrove forest, coral, and sea grass habitats. The northwestern part of Nayband marine park is limited to the village of "Bidkhon" and oil and gas industries (Pars Special Economic Energy Zone, PSEEZ). The discovery and exploitation of PSEEZ have led to the establishment of vast and pollutant industries, such as petrochemical complexes, gas refineries, power plants, storage tanks, and export wharves.

The stations considered in this study are illustrated in Table 1 and Fig. 1. Sampling procedures of sediments were carried out according to guidelines of MOOPAM (2000), recommended for the analysis of marine sediments. Surface sediment samples (0–5 cm) were taken during winter 2022 (January) using the Van Veen grab (made of stainless steel, overall dimensions approximately 20 × 30 × 60 (cm) and weight 5 kg) with three repetitions. The samples were placed in solvent-cleaned containers and stored at 4 °C. Until analysis, samples were stored at − 20 °C in the laboratory. Table 1 shows the geographic distribution of grain size and total organic matter (TOM). Grain size analysis exhibited

Table 1 Location of sampling sites, total organic matter (TOM%) and grain size fraction of each site

Stations	Latitude	Longitude	TOM (%)	Sand (%)	Mud (%)
NB1	27.446023	52.656113	4.25	39.95	60.05
NB2	27.411862	52.64812	4.5	15.42	84.58
H1	29.144895	50.64383	11.25	4.92	95.08
H2	29.133812	50.633921	2.0	99.87	0.13
M2	28.15305	51.291272	8.0	8.10	91.90
M1	28.149956	51.461137	3.0	6.46	93.54
NL1	27.851254	51.522387	5.5	69.36	30.64
NL2	27.792698	51.480302	2.5	94.12	5.88

that most of the sediments consist of two textural classes, sand and mud (silt + clay).

Sample analysis

To measure the trace metal concentration levels in sediments, samples were freeze-dried for 48 h and sieved through a 63-µm sieve (Ravisankar et al. 2018). One gram of sieved sediment was poured into a round bottom flask and refluxed with 5 mL of concentrated HNO_3 (Merck) and shaken for 2 min, and then, 2 mL of concentrated HCl was added, and the shaking was continued. The samples were digested by a hot plate for 2 h. Digested and cooled samples were filtered and brought to volume with deionized water into a 50-mL volumetric flask. The trace metal concentrations were measured using an inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900).

For PCB, PAH, and TPH analysis, immediately after collection, sediments were freeze-dried for 48 h and then ground and sieved through a 250-µm stainless steel sieve. For PCB and TPH analyses, 5 grams of the granulated sample was transferred to two 40-mL vial and 60 µL of PCB-209 (10 ppb), and p-Terphenyl-d14 (128 ppb) was added to PCB and TPH samples as internal standard, respectively. Sediment samples were extracted three times with 20 mL of a mixture of dichloromethane and acetone (1:1) in an ultrasonic bath for 5 min and centrifuged at 1500 rpm to separate sediment from the solvent extract, and the extraction solvents were collected in a 100-mL rotary flask. For complete extraction of PCBs and TPHs, extraction and decantation steps were repeated three times. Then, the eluted solution was concentrated and replaced by hexane to 5 mL with a rotary evaporator. Finally, 1 µL of the resulting solutions was injected into GC-MS (GC 6890 Agilent MS 5973N, Mode EI) to analyze the concentration levels of PCB and TPH compositions.

The extraction of PAHs from sediment samples followed the method of Rhind et al. (Rhind et al. 2009). Five grams of the sieved samples (dry weight) was added with surrogate standards (D10-acenaphthene (Ace-d10), D10-phenanthrene (Phe-d10), D12-benzo[a]pyrene (BaP-d12)) and 8 mL ethanolic potassium hydroxide (1 mol/L). The samples were heated (90 °C for 8 h), and the analytes were extracted by hexane, purified with a column packed with activated silica gel, and topped with 1 cm anhydrous sodium sulfate. Then, elution of the PAHs was carried out with dichloromethane/hexane (1:4, v/v). The eluted solution was concentrated and replaced by 1 mL of hexane with a rotary evaporator and stored at 4 °C for further analysis (Wang et al. 2014).

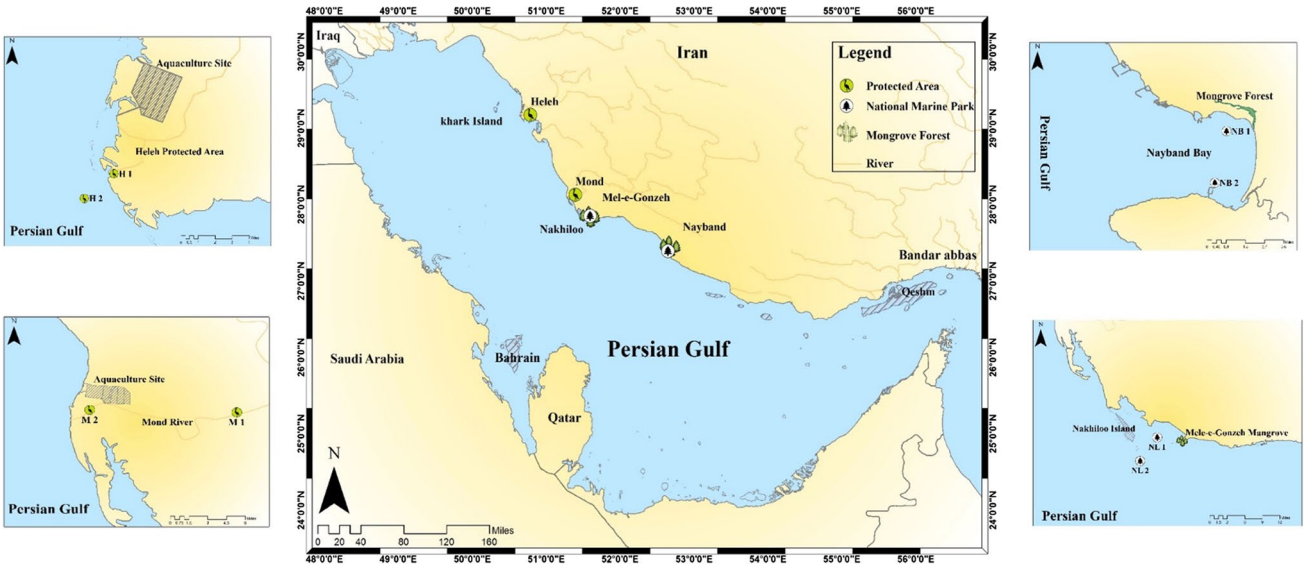

Fig. 1 The location of sampling stations within the marine protected areas that are spread across the northern Persian Gulf (Bushehr Province, Iran)

GC-MS (GC 6890 Agilent MS 5973N, Mode EI) was used to measure the concentration levels of PAHs. Total organic matter in sediments was determined by ignition loss. Ten grams of dry sediment (105 ± 2 °C until constant weight) was heated in a muffle furnace at 450 °C for 4 h (Commendatore et al. 2000).

Quality control and quality assurance

Appropriate replicates were analyzed together with certified reference materials (CRM), ensuring the precision and accuracy of the analytical procedures throughout the laboratory analyses. The quality assurance of the analytical results of HMs, PAHs, and PCBs was controlled with the use of a certified sediment reference materials including IAEA-405, IAEA 408, and IAEA-159, respectively. The results of the quality control showed a good agreement with the certified value and CRM recovery values were between 87 and 103% for HMs, 85–104% for PAHs, and 75.3–102.7% for PCBs. The precision of replicate measurements was better than about 12% for PAHs, 10% for HMs, 6% for PCBs, and 15% for TPHs. Inter-laboratory tests were also performed for several samples to confirm the methodology and result.

Statistical analyses

Statistical analyses were carried out using SPSS (version 26). To determine the significant differences between the stations, ANOVA and Tukey post hoc analyses were carried out. The p-value of < 0.05 was considered statistically significant between the data. PCA and CA, as well as Pearson's correlation coefficient analysis (R), were performed using the PAST software (version 4.13) to categorize the variables in similar groups and investigate their environmental source/behavior. The raw data were normalized before running PCA and CA.

Results and discussion

PAH analysis

PAH compounds are an important group of POPs containing two or more condensed aromatic rings. PAHs tend to be associated with organic carbon in aquatic media due to their hydrophobicity and then deposited in sediments which are their major reservoirs in the marine environments (Abdollahi et al. 2013; Barakat et al. 2013). The Environmental Protection Agency (USEPA) involved 16 PAHs as precedence control pollutants (Criteria and Office 1993), and over half of these PAHs are potentially carcinogenic to humans, according to the International Agency for Research on Cancer (IARC) (Cancer 2010) and the USEPA.

The mean concentration levels of 16 PAHs (µg/kg) in sediment samples of different MPAs are presented in Table 2. The mean levels of naphthalene, fluorene, phenanthrene, pyrene, and benzo(a)pyrene in different stations were statistically significantly different (p-value < 0.05). Results showed that total concentrations of 16 PAHs varied from 4.65 to 20.86 µg/kg dry weight (dw) (Table 2). The highest concentrations of Σ_{16}PAHs were detected in station M2 (20.86), followed by station H1 (17.80), while the lowest concentrations were found in station NB1 (4.65), followed by M1 (6.0). M2 and H1 located in the Mond and Helleh Estuary mouth, respectively. Adjacent agricultural and aquaculture fields can be one of the reasons for the increase of PAHs in these stations. Also, there are motorboat fishing activities that PAHs could be released due to the accidental petroleum spills of a boat, discharge of fuel, or motorboat residues. Added to this, the discharge from the Mond and Helleh rivers might also have a role in this increase. Additional research will be required to assess and compare the contribution of these factors in the Mond and Helleh MPAs. According to Montuori et al., different sources can contribute to the formation of PAHs in the marine environment, which includes industrial effluents, sewage, oil spills, runoff, and atmospheric fallout (Montuori et al. 2022).

The PAH composition and distribution in the sediments are influenced by sediment characteristics such as TOM content and grain size (Baran et al. 2017). Stations H1 and M2 (Table 1) displayed a predominance of fine sediments (mud), with values higher than 90%, and lower content of larger particles (sand). The higher PAH concentration detected in these stations corresponded to the higher fine fraction content in the samples (mud). Also, the highest TOM content (Table 1) was found in these stations suggesting that TOM plays an essential role as a driver of PAH accumulation in these points.

Ecological quality status is classified into three levels according to TOM content: high-good (< 5%), moderate (5 to 10%), and poor-bad (> 10%) (Marin et al. 2008). As shown in Table 1, station H1 indicated a poor-bad quality and station M2 showed a moderate quality, while the remaining indicated a high quality.

The PAH concentrations in this study were lower than those reported in sediments from other MPAs worldwide. The PAH concentrations in sediments from Goiana Estuary, Brazil, were < LOD—156.4 µg/kg (de Arruda-Santos et al. 2018); < LOD—180.6 µg/kg in Mosaic of MPAs of Sao Paulo State, Brazil (Moreira et al. 2019); 0.7 to 140 µg/kg in Spain (Cortazar et al. 2008); and 2.94–199.08 µg/kg in St. John, US Virgin Islands (Whitall et al. 2015). In a study by Perra et al. (2011), the total PAH concentrations ranged from 0.71 to 1550 µg/kg in surface sediment from 15 Italian MPAs (Perra et al. 2011). In another study by Oliva et al. (2020), the total concentration of the PAHs in MPAs within

Table 2 The mean concentrations levels of PAHs (μg/kg) in sediments of marine protected areas

PAHs	M1	H2	NL1	NB1	NB2	NL2	M2	H1	*p*-value	LOD	LOQ
Naphthalene	< LOD	3.21	< LOD	< LOD	5.74	3.81	8.08	4.63	0.045	0.464	1.547
Acenaphthylene	0.03	0.09	< LOD	< LOD	0.06	0.05	0.15	0.04	0.125	0.008	0.028
Acenaphthene	< LOD	< LOD	1.40	< LOD	< LOD	< LOD	< LOD	1.10	0.545	0.321	1.070
Fluorene	< LOD	< LOD	1.78	< LOD	0.84	< LOD	< LOD	1.02	0.048	0.044	0.15
Phenanthrene	0.71	0.72	2.32	0.58	0.85	0.72	0.91	0.76	0.015	0.046	0.152
Anthracene	0.59	0.75	0.74	0.54	0.92	1.04	1.20	1.10	0.063	0.074	0.247
Fluoranthene	0.41	0.59	1.91	0.31	0.44	0.28	0.40	0.83	0.055	0.018	0.060
Pyrene	1.49	5.03	2.60	1.49	1.77	1.28	1.42	1.96	0.008	0.025	0.082
Benz(a)anthracene	0.29	0.24	0.11	0.31	0.24	0.26	0.32	0.25	0.112	0.011	0.036
Chrysene	0.19	0.11	< LOD	0.09	0.08	0.11	0.18	0.08	0.088	0.015	0.050
Benz(b)fluoranthene	0.27	0.26	< LOD	0.16	0.20	0.46	0.76	0.50	0.064	0.044	0.148
Benzo(k)fluoranthene	0.14	< LOD	< LOD	< LOD	< LOD	0.11	0.14	0.14	0.077	0.03	0.094
Benzo(a)pyrene	1.87	1.68	0.56	1.17	1.53	4.10	7.29	4.69	0.004	0.03	0.107
Indenol (1.2.3-cd)pyrene	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.37	0.061	0.07	0.248
Dibenzo(a,h) anthracene	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.215	0.10	0.336
Benzo (g.h.I) perylene	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.30	0.111	0.09	0.300
An/(An+ Phe)	0.45	0.51	0.24	0.48	0.52	0.59	0.57	0.59	-	-	-
Flu/ (Py + Flu)	0.22	0.10	0.42	0.17	0.20	0.18	0.22	0.30	-	-	-
LMW/HMW	0.29	0.60	1.20	0.32	1.97	0.85	0.98	0.95	-	-	-

the Argentinean Continental Shelf ranged from 19.47 to 183.17 μg/kg and low molecular weight PAHs (anthracene and naphthalene) were predominant (Oliva et al. 2020). In Yim et al.'s (2007) study, total concentrations of PAHs were in the range of 8.80–18,500 μg/kg, and industrialized and urbanized areas exhibited a high amount of PAHs (Yim et al. 2007). In a study conducted by Aghadadashi et al. (2019b), the levels of $\sum_{16}$PAHs in surface sediments of Iranian coast of the Persian Gulf were in the range of 1.98–814 ng/g dw and confirmed that PSEEZ adjacent to the Nayband National Park is the hot zone of PAH pollution. The profile of PAHs was mainly composed of 2,3-ring chemicals and suggested a local source of PAHs and relatively fresh inputs. Total PAH concentrations in intertidal zones of the northern Persian Gulf (Asaluye), which is in the vicinity of the Nayband National Park, have been evaluated in September 2016 (Keshavarzifard et al. 2018). The levels of ∑16PAHs varied from 12.8 to 81.2 μg/kg dry weight in sediment, which can be categorized as low level of pollution.

The previous PAH monitoring studies mainly focused on the polluted coastal region and industrialized and urbanized areas, and MPAs have received less attention. Due to the ecological importance of MPAs in protecting critical habitats and representative samples of maritime life and assisting in restoring the productivity of the oceans and avoiding more degradation, continuous monitoring of these areas is necessary.

Considering all samples, the composition patterns of 16 priority PAH congeners are as follows: 5-ring > 2-ring > 4-ring > 3-ring (see Fig. 2). The 6-ring PAHs were not seen in any of the stations (except station H1 in a small amount). Comparing the concentration levels of PAHs in sediment samples based on the frequency of rings showed that the distribution patterns are different among the studied stations (Fig. 2). The 4- and 5-ring PAHs were most dominant in stations M1, M2, H1, H2, NL2, and NB1. In contrast, the 2- and 3-ring structures were highest in stations NL1 and NB2. In general, petrogenic PAHs (e.g., from fossil fuels) present dominance of compounds with lower molecular weight PAHs-LMW (2-3 rings), while pyrogenic PAHs (e.g., those produced by burning processes) are dominated by higher molecular weight PAHs-HMW (4-6 rings) (Oliva et al. 2020). To expand this analysis, a molecular-ratio approach was applied to address pyrogenic and petrogenic sources. The following ratios were used: fluoranthene/(pyrene + fluoranthene), anthracene/(anthracene + phenanthrene), and LMW/HMW. Fluoranthene/(pyrene + fluoranthene) values < 0.40 suggest petroleum origin, whereas values > 0.4 are indicators of combustion. Furthermore, values between 0.40 and 0.50 show liquid fossil fuel combustion, while ratios higher than 0.50 are attributable to biomass combustion (Yunker et al. 2002). For anthracene/(anthracene + phenanthrene) ratios, pyrogenic sources indicate values higher than 0.10, whereas petrogenic PAHs show values < 0.10. Lastly, LMW/HMW ratios < 1 indicate pyrogenic source whereas values > 1 present petrogenic source (Yuan et al. 2001; Yunker et al. 2002). Table 2 shows the ratio of An/(Phe + An) > 0.1 for all locations, Flu/ (Flu + Py) <

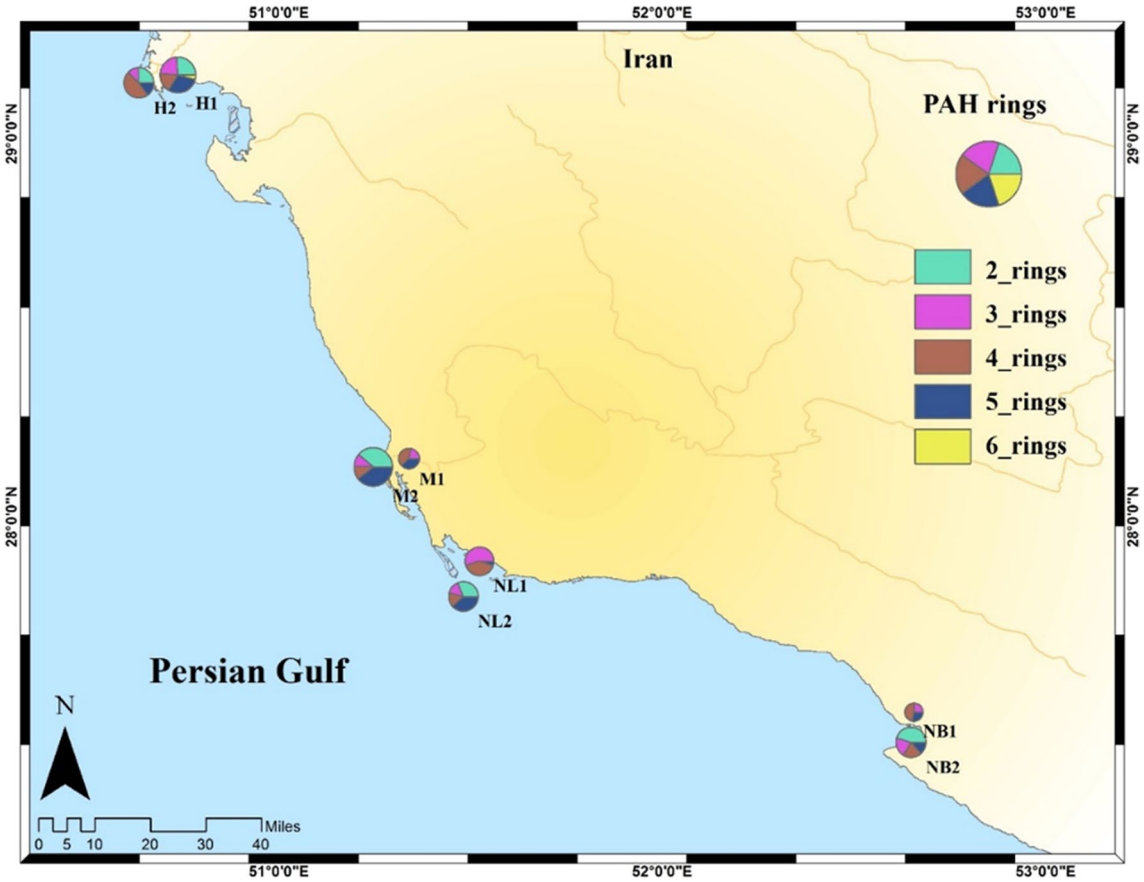

Fig. 2 The distribution pattern of PAHs in sediments at the different sampling locations. Different colors indicate distribution of PAHs according to the number of rings at each site

0.40 (except NL1), and LMW/HMW < 1, indicating that the primary PAH source was mainly from pyrogenic origin. Only NL1 and NB2 present values of LMW/HMW > 1, which showed a petrogenic source at these sampling sites. Considering the PAH molecular ratios and ring's pattern, a mixed source with a pyrogenic fingerprint dominance was detected for sediments of the Persian Gulf's MPAs. The mixed source for PAHs in this study is in agreement with the sources of deposited PAHs in the northern Persian Gulf, Iran's environmentally hot zones (Aghadadashi et al. 2019b), and intertidal zones of Asaluyeh (Keshavarzifard et al. 2018).

All PAHs had lower concentrations than the effects range-low (ERL) and effects range-median (ERM) values suggested by Long et al. (Long et al. 1995). The concentration levels of individual PAHs in our study varied from < LOD to 8.08 µg/kg and were much lower than both of the ERL and ERM values (Table S1).

TPH analysis

Results showed that the spatial distribution of TPH compound in the sediments was not homogenous and varied from 5.21 to 17.90 µg/g dw (Table 3). The mean concentrations of TPHs in different stations were statistically significantly different (p-value < 0.05). The highest value of TPHs were found at stations M2 (17.90 µg/g dw) and H1 (15.94 µg/g dw), located in the Mond and Helleh Estuary mouth, respectively. The lowest levels were detected at the station NL1 (5.21 µg/g dw). The different pattern indicates the contribution of the anthropogenic sources to the TPH loads in the MPAs' coastal water. These sources may include adjacent agricultural and aquaculture activities, motorboat fishing activities, occasional oil spills, and land-based runoffs from Mond and Helleh rivers. Also, the results showed that TOM and a fine fraction of sediments (mud) were effective parameters in controlling the alteration of TPH in the stations M2 and H1. Smaller particles of sediments (e.g., muddy sediment) frequently indicate more organic content and accumulate more organic pollutants (Massoud et al. 1996).

Massoud et al. (1996) proposed that TPH contents in sediment of the Regional Organization for the Protection of the Marine Environment (ROPME) Sea Area in the range of 10 to 15 µg/g and 15 to 50 µg/g should be considered

Table 3 Mean concentrations of TPHs (μg/g) and hydrocarbon indexes in the sediment for individual hydrocarbon

TPHs	M1	H2	NL1	NB2	NL2	NB1	M2	H1
C10	0.001	0.121	0.000	0.232	0.178	0.000	0.138	0.212
C11	0.000	0.005	0.000	0.001	0.002	0.000	0.005	0.004
C12	0.002	0.268	0.003	0.439	0.445	0.000	0.524	0.418
C13	0.000	0.008	0.005	0.007	0.005	0.000	0.006	0.008
C14	0.105	0.371	0.116	0.467	0.518	0.060	0.550	0.449
C15	0.001	0.003	0.003	0.001	0.002	0.001	0.003	0.003
C16	0.188	0.189	0.096	0.206	0.230	0.207	0.248	0.201
C17	0.002	0.003	0.003	0.005	0.003	0.005	0.003	0.003
C18	0.169	0.132	0.072	0.147	0.157	0.180	0.179	0.144
C19	0.001	0.002	0.001	0.002	0.002	0.002	0.002	0.002
C20	0.121	0.089	0.049	0.097	0.106	0.125	0.126	0.095
C21	0.005	0.004	0.002	0.004	0.004	0.005	0.005	0.005
C22	0.073	0.056	0.030	0.060	0.066	0.077	0.078	0.061
C23	0.007	0.005	0.003	0.005	0.006	0.003	0.008	0.006
C24	0.054	0.043	0.024	0.046	0.050	0.059	0.057	0.047
C25	0.011	0.010	0.006	0.011	0.012	0.012	0.014	0.012
C26	0.051	0.041	0.022	0.043	0.047	0.055	0.055	0.046
C27	0.022	0.015	0.009	0.016	0.016	0.019	0.020	0.022
C28	0.083	0.066	0.033	0.067	0.070	0.082	0.083	0.068
C29	0.070	0.027	0.019	0.030	0.028	0.034	0.048	0.075
C30	0.063	0.046	0.026	0.046	0.052	0.052	0.054	0.050
C31	0.061	0.014	0.016	0.020	0.020	0.019	0.036	0.063
C32	0.046	0.037	0.019	0.037	0.040	0.033	0.042	0.034
C33	0.034	0.010	0.007	0.010	0.011	0.010	0.021	0.031
C34	0.020	0.018	0.008	0.016	0.018	0.010	0.017	0.013
C35	0.009	0.009	0.003	0.009	0.008	0.006	0.011	0.010
C36	0.007	0.008	0.003	0.007	0.008	0.004	0.007	0.005
TPH concentration	11.51	17.9	10.27	15.19	15.94	12.56	5.21	15.89

unpolluted and slightly polluted, respectively. Moreover, TPH concentrations that are less than 15 μg/g dw were considered the natural background levels for bottom sediment by ROPME (de Mora et al. 2010). According to these classifications, the sediment samples in Bushehr Province's MPAs were categorized between unpolluted and slightly polluted areas. Thus, stations M2, H1, NL2, and NB2 can be considered vulnerable stations. According to de Mora et al. (2010), concentrations of TPHs in sediments collected in Bushehr were 318 μg/g and no evidence of contamination was observed in sediments from the Mond River site in 2005.

Based on Arzaghi et al.'s (2018) study, ecological risk assessment was done (Arzaghi et al. 2018). The hazard quotient (HQ) ≥ 1 indicates high risk; (HQ) < 1 is medium risk; and (HQ) < 0.1 indicates low risk (Tian et al. 2020). HQ is obtained by dividing the measured environmental concentration of specific hydrocarbon by the toxicity reference value. The toxicity reference values for sediment were 5.54 mg/kg for C14–C18 and 9.88 mg/kg for C19–C36 (Mean and Log 2007). The values of HQ are less than 1 in all stations (Table 3).

The concentration of TPHs in the current study was compared with the results of other regions with similar climate. The concentration of TPH in the studied area is significantly lower than the surface sediments of Imam Khomeini port (32.73–97.15 μg/g dw), a semi-closed ecosystem with limited connection to the PG (Jazani et al. 2013). Due to the extensive activity and high traffic of vessels carrying fuel and other export goods in this port, as well as the lack of its self-remediation capacity, the concentration of suspended solids and pollutants was high. The TPH concentrations in the Musa Bay (northwest of PG) sediments varied from 16.48 to 97.15 μg/g dw with the mean value of 48.98 ± 30.36 μg/g dw (Jazani et al. 2013). The highest concentrations were detected in stations adjacent to the coastline, which were affected by severe petrochemical discharges and shipping activities. The concentration of TPH in sediments of the PG and Omani waters varied between 0.134 and 48,018 μg/g dw (Uddin et al. 2021). The TPH detected

values ranged from 7.43 to 458.61 μg/g in the sediments of Kuwait's coastline (Metwally et al. 1997).

The concentrations obtained in the current study are relatively higher than the concentration of TPHs of the northern parts of the Oman Sea, 0.10–4.10 μg/g dw (de Mora et al. 2010); Arvand River, 2.46–3.83 (Al-Saad 1995), coastline (ND to 1.71 μg/g dw) and mangrove (0.2 to 0.63 μg/g dw) sediments of the northern PG (Mohebbi-Nozar et al. 2015); and Tiab mangroves, Hormozgan province, Iran, 0.36 to 4.89 μg/g (Zahedi Dehuii et al. 2019). Globally, the TPH levels in the sediments of this study were significantly lower than those from other coastal areas like Algoa Bay in the Eastern Cape Province of South Africa (0.72 to 27.03 μg/g) (24); Newark Bay Estuary, New Jersey, USA (240 to 280 μg/g) (Huntley et al. 1995); and Barnegat Bay-Little Egg Harbor Estuary, New Jersey (47 to 1003 μg/g) (Vane et al. 2008). However, sediment from a few other places around the world discovered TPH concentrations that were comparable to those reported in the present study. Examples include those from Todos os Santos Bay, Brazil, 1.60 and 10.60 μg/g dw (de La Habana 2009).

PCB analysis

Eighteen PCB congeners, including eight mono-ortho-PCBs 189, 167, 157, 156, 123, 118, 114, and 105; four non-ortho-PCBs 169, 126, 81, and 77; and six indicator PCBs 180, 153, 138, 101, 52, and 28, were measured since they are the most toxic compounds and have a common mode of function. The mean concentrations of 18 PCBs (ng/g dw) in sediments of different MPAs are presented in Table S2. The highest concentration of ΣPCBs is at NL2 (0.419 ng/g dw), followed by NB1 (0.413 ng/g dw), and the lowest concentration of PCBs is observed at H2 stations (0.345 ng/g dw). Among the 18 PCB congeners analyzed, the main components correspond to PCB-77, PCB-105, PCB-81, PCB-101, and PCB-114 (Fig. 3). The mean levels of PCB-28, PCB-52, PCB-123, PCB-118, PCB-157, and PCB-169 in different stations were statistically significantly different (p-value < 0.05). The mean concentration of $\sum_{18}$PCB measured in the surface sediments of different MPAs (0.345–0.419 ng/g dw) was low compared to other marine environments such as Lake Chapala, Mexico (9–27 ng/g dw) (Ontiveros-Cuadras et al. 2019); San Diego Bay, southern California (23–1387 ng/g dw) (Neira et al. 2018); Pearl River Estuary, China (17.68–169.26 ng/g dw) (Zhao et al. 2016); Pearl River Delta, China (16.15–477.85 ng/g dw) (Wang et al. 2019); the coastal area of Bangladesh (32.17–199.4 ng/g dw) (Habibullah-Al-Mamun et al. 2019); Southern Yellow Sea (0.51–5.84 ng/g dw) (Zhang et al. 2007); Bengal Bay, India (0.019–6.5 ng/g dw) (Rajendran et al. 2005); Hugli estuary, India (0.18–2.33 ng/g dw) (Guzzella et al. 2005); coastal surface sediment, Hormozgan Province, Iran (0.88–461.97 ng/g dw) (Nozar et al. 2014); and Larak Island, Iran (2.95 to 7.95 ng/g dw) (Ranjbar Jafarabadi et al. 2019). Our results indicated that the sediments collected from the studied MPAs were much less polluted than Shadegan Wetland, Khuzestan Province, Iran, which is known as one of Iran's industrial polluted zones. The total of 7 congener concentrations of PCBs in sediment of 4 stations around Shadegan wetland protected area in the northwestern PG was from 3400 to 50200 ng/g dw, and the mean value was 18220 ng/g dw (Zahed et al. 2009).

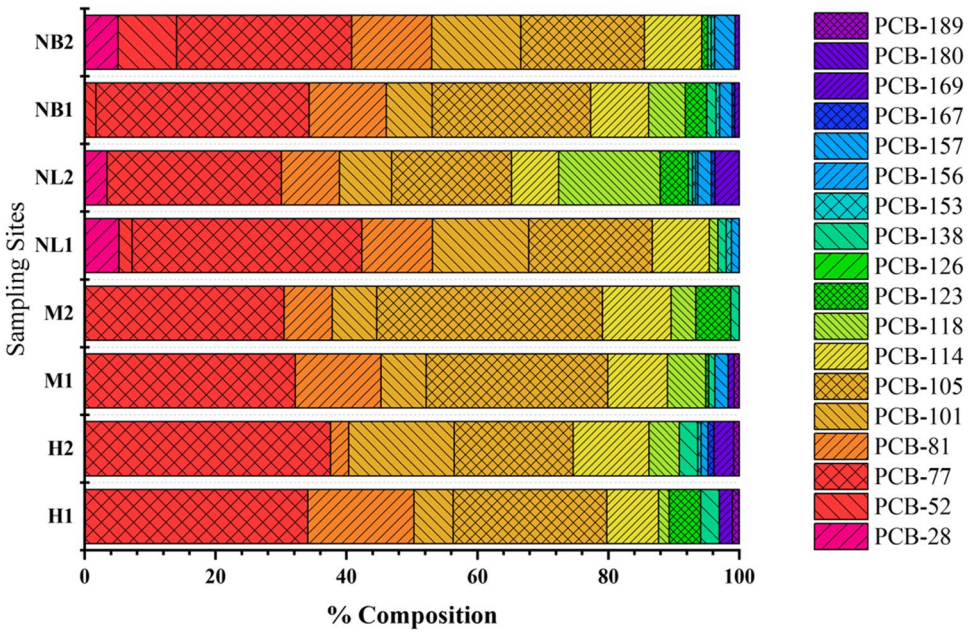

Fig. 3 The composition pattern (%) of PCBs (ng/g) in sediments of the different sampling sites

However, the concentrations of PCBs were comparable to values reported in Tokyo Bay, Japan (0.04–0.64 ng/g dw) (Kobayashi et al. 2010); Laguna de Terminos, a protected area of the coast of Campeche, Mexico (0.016–0.36 ng/g dw) (57); Belgian coastal harbors (0.03–3.1 ng/g dw) (Monteyne et al. 2013)' and Liaohe River protected area, China (0.08–0.36) (55). Arfaeinia et al. (2017) investigated levels of PCBs in the sediments of Asaluyeh harbor, the northern PG. The average concentrations of $\sum_{18}$PCB were 0.51, 0.14, and 0.031 ng/g dw for the industrial, semi-industrial, and urban stations, respectively (Arfaeinia et al. 2017). The ∑PCB values in Bushehr and the Mond River sediments in 2005 were 0.616 pg/g and 0.036 pg/g dw, respectively (de Mora et al. 2010).

Heavy metal analysis

Trace metals in sediments and seawater can be absorbed by aquatic organisms directly. Subsequent accumulation within their bodies may be magnified through the food chain, thus threatening the marine ecosystem and human health (Zhang et al. 2015). The average concentration levels of trace metals in sediments of different MPAs are presented in Table 4. The concentration of metals ranged as follows: Arsenic (As), 4.79–9.69; cobalt (Co), 2–12 µg/g; chromium (Cr), 39–142 µg/g; nickel (Ni), 18–90 µg/g; vanadium (V), 15–58 µg/g; magnesium (Mn), 184–425; lead (Pb), 7–45.9 µg/g; zinc (Zn), 6–42.4 µg/g; copper (Cu), 4–20; aluminum (Al), 0.75–4.12%; and iron (Fe), 0.35–1.62%. The concentration of cadmium (Cd), silver (Ag), molybdenum (Mo), and mercury (Hg) was below the limit of detection. The mean levels of Co, As, Cr, Cu, Mn, Ni, V, Al, and Zn in different stations were statistically significantly different (p-value < 0.05). Mn, Cr, Zn, and Pb were the primary trace metals in sediments of the studied MPAs. The highest concentration for most of the trace elements was found in sediments from station H1 followed by M1 and NL1, and the lowest concentration was at station NB2. Agriculture and aquaculture are the most important activity in H1 and M1 area. A similar finding was attained by Guo et al. (2021), that the principal source of contamination of Cd, Zn, Pb, and Cr was agriculture. Long-term usage of phosphate fertilizer will result in the accumulation of Pb and Cr, which also occur at high levels in fertilizers (Guo et al. 2021).

The high concentration of trace metals in the stations located in the Helleh Estuary (H1) and Mond River (M1) could be caused by the high percentage of small mud particles in these stations (Table 1). Fine-grained sediments, with higher surface-to-volume ratios, have more potential to remove inorganic and organic pollutants from the water column. Generally, fine sediments with more organic content keep more pollutants than moderately coarse sand sediments (De Mora and Sheikholeslami 2002). Metwally et al. (1997) stated the highest concentration of nickel and vanadium in the coastal sediments of Kuwait was related to the stations whose sediments were muddy (Metwally et al. 1997).

According to the US Environmental Protection Agency (Table 4), the stations NL1, M1, M2, and H1 have recorded a high degree of Cr and Ni contamination and the other stations indicated moderate contamination. The Cr concentration was higher than the ERL but lower than the ERM values. The concentration of Mn in the sediments of NL1, M1, M2, and H1 with moderate contamination is significant. The stations NB2 and H2 showed a high level of As contamination, and the other stations indicated moderate contamination.

Trace metal concentrations in the current study were compared with other regions in the PG, other parts of the

Table 4 The mean concentration levels of trace metals (µg/g) and Al and Fe (%) in sediments collected from marine protected areas

Stations	Ag	As	Al	Fe	Mo	Cd	Co	Cr	Cu	Hg	Mn	Ni	V	Pb	Zn
NB2	< LOD	8.25	0.75	0.35	< LOD	< LOD	2	45	4	< LOD	184	18	15	9	7
H1	< LOD	6.02	4.12	1.62	< LOD	< LOD	12	103	20	< LOD	352	90	58	9	37
H2	< LOD	9.69	0.76	0.44	< LOD	< LOD	3	39	5	< LOD	222	20	16	7	6
M2	< LOD	5.33	2.77	1.15	< LOD	< LOD	9	142	13	< LOD	400	61	42	8	26
M1	< LOD	4.79	3.36	1.31	< LOD	< LOD	10	83	17	< LOD	425	73	47	9	28
NL1	< LOD	6.21	3.08	1.28	< LOD	< LOD	9	120	16	< LOD	381	67	47	45.9	42.4
Mean	-	6.71	2.47	1.02	-	-	7.50	88.67	12.50	-	327.33	54.83	37.50	14.65	24.4
ERL[a]	1.0	8.2	-	-	-	1.2	-	81	34	0.15	-	20.9	-	46.7	150
ERM[a]	3.7	70	-	-	-	9.6	-	370	270	0.71	-	51.6	-	218	410
Not polluted[b]	-	< 3	-	-	-	-	-	< 25	< 25	-	< 300	< 11	-	< 40	< 90
Moderately polluted[b]	-	3-8	-	-	-	< 6	-	25–75	25–50	-	300–500	12–56	-	40-60	90-200
Heavily polluted[b]	-	>8	-	-	-	> 6	-	> 75	> 50	-	> 500	> 57	-	> 60	> 200

[a]ERL and ERM for trace metals (µg/g) recorded in sediment according to Long et al. (Long et al. 1995)

[b]US Environmental Protection Agency (Agency 1987)

world, and some standards of other countries (Table S3). The mean concentrations of Zn, Cr, Co, Ni, Mn, and V from our studied area were lower than those of sediments from Kuwait (Basaham and Al-Lihaibi 1993). The Fe concentration in the current study was lower than in the Strait of Hormuz, Kuwait, Bidkhun mangrove, and Black Sea, but more than in Nayband Bay, Bostaneh, Saudi Arabia, and Bahrain/Qatar (Table S3). The average Fe concentration was less than existing guidelines, as well (Guidelines for Metals in sediments, SEL and LEL).

The Co concentration in this study was less than its concentration in Kuwait and Mahshahr but higher than coastal sediments of the PG, Saudi Arabia, and Bahrain/Qatar. The concentration of As was consistent with the result of an earlier study in the coastal sediments of the PG by de Mora et al. 2004.

The As concentration was lower than Bidkhun mangrove, Guidelines for Metals in sediments (SEL), and Primary and Secondary China National Standard (Table S3). Unpolluted coastal sediments usually have As concentrations of 5–15 µg/g (Neff 1997). The Cr concentration was more than protected areas in Poland, Saudi Arabia, and Bahrain/Qatar and lower than in the coastal sediments of the southern part of the PG and Kuwait. Cu concentration was more than its concentration in the region (Bushehr, Strait of Hormuz, Saudi Arabia, Bahrain/Qatar) but lower than the global standards mentioned in Table S3. Ni concentration was lower than SEL, Mahshahr (Iran), and Kuwait but higher than LEL, coastal sediments of southern PG, Saudi Arabia, Bahrain/Qatar, Nayband Bay, Strait of Hormuz, Bostaneh (Iran), and other regions far from the PG (Black Sea, Red Sea, protected areas, Poland). The average Ni concentration in the studied sediment (54.83 µg/g) was close to the adjacent region of Bidkhun mangrove (56 µg/g).

The mean concentration of V was more than the concentrations achieved in the other places of the PG, such as coastal sediments of southern PG, Saudi Arabia, and Bahrain/Qatar. Other studies have shown more concentration of V in Nayband Bay, Bidkhun mangrove, and Kuwait. According to some standards including, Primary China National Standard, Secondary China National Standard, Guidelines for Metals in sediments (LEL and SEL), and Canadian sediment quality guidelines (TEL), the mean Pb concentration in all studied stations was lower than the standard level (Table S3). The mean Pb concentration in this study was lower than its concentration in other marine regions (Bidkhun mangrove, Nayband Bay, Strait of Hormuz, Mahshahr, and sediments of southern PG) but higher than Bushehr and Bostaneh (Iran). The higher concentration of Pb in station NL1 can be caused by the fossil fuels used for fishing and recreational motor vessels. Lead is also present in paint combinations, including the colors used for the hulls of ships and boats (CCREM 1987). The mean Zn concentration in all studied stations was lower than its levels in other marine regions and global standards. Relatively high concentrations of Pb and Zn were observed in station NL1, supporting the hypothesis of a point source of pollution at this station, the effects of which reduce with distance from the source.

Sedimentary levels of heavy metals must not be used alone as indicators of pollution status in marine environments such as the Persian Gulf, but rather in combination with other geochemical, statistical, and ecological techniques (Al-Abdali et al. 1996). In this sense, quantitative geochemical methods, such as the non-dimensional enrichment factor, can discriminate natural and background sources of heavy metals.

Enrichment factor (EF) has been used to assess heavy metal contamination and to determine sedimentary metal source produced by anthropogenic events or natural origin, which normalizes metal concentrations according to the sediment texture properties (Neyestani et al. 2016). In this index, aluminum is widely used, indicating aluminum silicate at coastal areas where this element is predominant. The EF is calculated as follows:

$$EF = (H/Al)s/(H/Al)c$$

where (H/Al)s/(H/Al)c are the relative concentrations of the examined heavy metal (H) and the aluminum contents in the samples and crust or deeper sediments, respectively.

In this study, we used background concentrations of metals in sediment of the northern Persian Gulf which are 10.84, 0.82, 96.82, 8.00, 22.13, 54.94, 68.14, 13.30, 101.69 ppm, 3.19%, and 2.4% for As, Cd, Ni, Pb, Cu, Zn, V, Co, Cr, Al, and Fe, respectively (Neyestani et al. 2016).

The elements are greatly from crustal materials if EF = 0.5–1.5 while the values higher than 1.5 indicate a deviation from geogenic distribution (1.5–2, minor enrichment; 2–5, moderate enrichment; 5–20, moderately severe enrichment; 20–40, severe enrichment; and > 40, very severe enrichment) (Aghadadashi et al. 2019a; Delshab et al. 2017).

The EF values for Cu, Co, Ni, V, and Zn were < 1.5 at all stations which indicated that these HMs were frequently released from natural origins (Table S4). Cr had an enrichment factor of 1.61–1.88 at stations NB2, M2, and H2, indicating minor enrichment and no enrichment at H1, NL1, and M1. The EF values for As show moderate enrichment at stations NB2 and H2 (EF, 3.24–3.75) and no enrichment at stations H1, M2, M1, and NL1. The EF values for Mn ranged between 2.84 and 3.43 at stations NB2 and H2 and 5.40 to 6.54 at stations H1, M1, M2, and NL1, respectively, implicating moderate to moderately sever enrichment. The highest EF value (21.08–34.11) was observed for Pb at stations NB2, H2, and NL1, indicating sever enrichment, while other stations show moderately sever enrichment (EF, 5.00–6.61). Thus, the results of Table S4 emphasized

that all studied stations were significantly affected by man-made loaded Pb and Mn. Pb is a toxic metal and its low concentrations might cause a threat to life in an aquatic environment when compared with other metals.

Multivariate statistical analysis

The Pearson correlation coefficient (R) can be used to measure the strength of a linear relationship between the contaminations. In addition, multivariate statistical analysis approaches, such as PCA and CA, have been widely applied to assess the level of contaminations in sediments (Mao et al. 2013). The PCA is used to reduce data and to extract a small number of latent factors for analyzing relationships among the observed variables (Lu et al. 2010). It is also employed to identify the source of contaminations in the sediments (Facchinelli et al. 2001). The CA is a statistical technique used to identify groups or clusters of similar sites based on similarities within a class and dissimilarities between different classes (Mishra et al. 2017).

The Pearson correlation coefficients for contaminations in sediments of the marine protected areas of the northern Persian Gulf are listed in Table 5. Most of the metal pairs show positive relations with each other. Elements V, Co, Ni, Cu, Zn, Al, and Fe show significantly positive correlation with each other. This may imply that these elements have a common origin. However, a relatively strong negative correlation was found between As with all other metals. Also, there were moderate positive correlations between PAHs-TPHs and PAHs-TOM. However, strong correlations were not found between PCBs with THPs or PAHs.

PCA was widely applied to identify sources of the contaminations in sediments by applying varimax rotation. The results of the eigenvalues and the factor loadings with a varimax rotation are listed in Table S5 and Table S6, respectively. The results show that the first four eigenvalues explain 94.03% of the total variance. The first factor explains 60.90% of the total variance and loads heavily on the heavy metals. Factor 2 is loaded primarily by PAHs and TPHs and accounts for 18.54% of the total variance (Table S5). Factor 3 is loaded primarily by PCBs (positive correlation) and As (negative correlation) and accounts for 8.38% of the total variance (Fig. 4). Also, factor 4 is loaded primarily by TOM and grain size fraction and accounts for 6.23% of the total variance.

The variables were normalized prior to CA, and then, Euclidean distances for similarities in the variables were calculated. Finally, hierarchical clustering by applying Euclidean distances was performed on the standardized data set. The CA results for the contaminations in sediments of the marine protected areas of the northern Persian Gulf are demonstrated in Fig. 5 as a dendrogram. Fig. 5 displays two

Table 5 Pearson's correlation coefficients between the variables (values in bold indicate significant correlation)

	TOM	Sand	Mud	PCB	PAH	TPH	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Sand	− 0.61237															
Mud	0.61237	− 1														
PCBs	0.075803	0.01971	− 0.01971													
PAHs	0.68511	− 0.26046	0.26046	0.39173												
TPHs	0.30469	− 0.31636	0.31636	0.29705	0.51441											
Al	0.654	− 0.4899	0.4899	0.72584	0.16368	− 0.08806										
As	− 0.45501	0.68115	− 0.68115	− 0.75105	− 0.06977	0.000596	**− 0.85943**									
Co	0.64599	− 0.46426	0.46426	0.76012	0.21087	− 0.05408	**0.99378**	**− 0.86166**								
Cr	0.63656	− 0.35979	0.35979	0.75148	0.48737	− 0.00646	0.74114	− 0.78837	0.77299							
Cu	0.60146	− 0.42456	0.42456	0.6637	0.095279	− 0.16761	**0.99574**	**− 0.83627**	**0.98768**	0.71014						
Fe	0.65489	− 0.43683	0.43683	0.71798	0.18614	− 0.11052	**0.99746**	**− 0.84103**	**0.99589**	0.76081	**0.99533**					
Mn	0.34578	− 0.37861	0.37861	0.66465	0.041875	− 0.17965	0.86758	**− 0.92477**	**0.89562**	**0.82069**	**0.86681**	**0.87308**				
Ni	0.65784	− 0.48053	0.48053	0.72796	0.173	− 0.08127	**0.9997**	**− 0.85007**	**0.99485**	0.73678	**0.99572**	**0.99808**	**0.86371**			
Pb	− 0.00977	0.38579	− 0.38579	− 0.27595	− 0.26013	− 0.85313	0.23706	− 0.16146	0.20309	0.3818	0.28415	0.26608	0.2765	0.22737		
Zn	0.57779	− 0.24822	0.24822	0.51409	0.097882	− 0.38617	**0.91366**	− 0.76639	**0.89776**	**0.80082**	**0.92476**	**0.9258**	**0.81871**	**0.90974**	0.60439	
V	0.66583	− 0.45305	0.45305	0.719	0.18881	− 0.11421	**0.99765**	**− 0.85013**	**0.99327**	0.77223	**0.99409**	**0.99908**	**0.87091**	**0.99741**	0.28467	**0.93456**

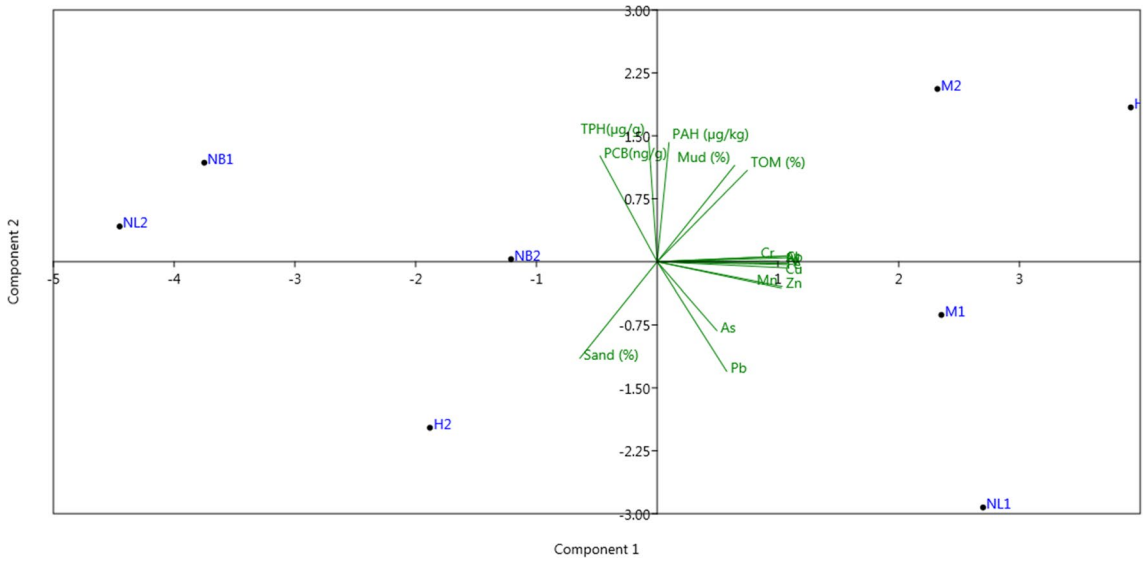

Fig. 4 PCA biplot of the variables

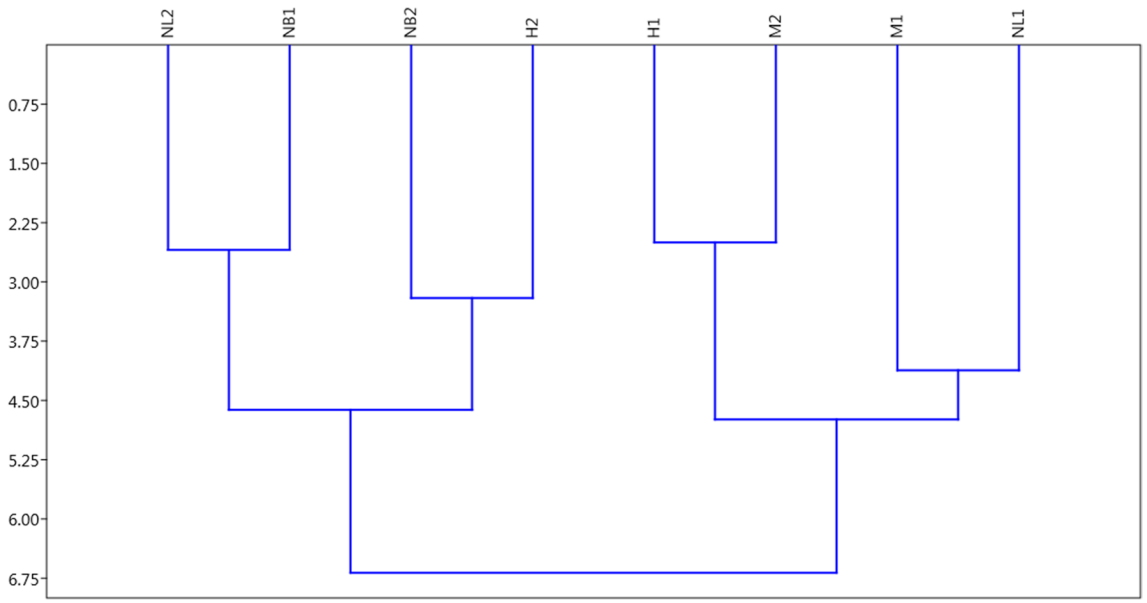

Fig. 5 Dendrogram results from Euclidean distances of hierarchical cluster analysis

clusters: (1) NL2, NB1, NB2, and H2; (2) H1, M2, M1, and NL1.

Conclusion

This first comprehensive study on the heavy metals and POP contamination in the sediments of MPAs along the northern Persian Gulf provides a reference for future studies of these compounds in the region. The results indicated that the levels of some contaminants in the MPAs are significant. There are adequate reasons to monitor the sources of pollutants and implement different policies to prevent pollutant entrance into water and sediments for prevention and reduction of ecological threats. According to the results of the current study, the Mond and Helleh Estuary mouth is an important hotspot (in most of the investigated pollutants including PAHs, TPHs, and heavy metals) in the area of study. The adjacent agricultural and aquaculture fields could be one of the reasons for this

finding. Also, there are motorboat fishing activities that PAHs could be released due to the accidental petroleum spills of a boat, discharge of fuel, or motorboat residues. Added to this, the discharge from the Mond and Helleh rivers might also have a role in this increase. Furthermore, the highest TOM content and higher fine fraction content in the sediments (mud) were found in these stations suggesting that sediment characteristics such as TOM content and grain size play a significant role in pollution accumulation in these areas. The EF values emphasized that all studied sites were significantly affected by man-made loaded Pb and Mn. The EF values indicated that Cu, Co, Ni, V, and Zn are frequently released from natural origins at all sites. Moreover, cluster analysis (CA) and principal component analysis (PCA) were also performed to summarize information of large data sets, because they offer better interpretation and understanding of water quality. The CA was performed on sampling site gained two groups, representing the possible similarity of pollution load at sampling locations in each group.

Based on our data, it can be concluded that the studied MPAs are not well protected from chemical contaminations. To have a precise understanding of the status and pressures on these marine areas, it is recommended to continue the ongoing pollution monitoring programs in these environments. Such information would be ultimately critical for developing robust science-based monitoring and reporting frameworks for MPAs across regional seas and environmental impact assessment of pollutants entering these areas.

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Data availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethics approval and consent to participate Not applicable.

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