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Assessment of pollution and ecological risk of heavy metals in the sediments of the western coast of Persian Gulf: A case study in Dayer port

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Abstract

Background: In recent years, the pollution of heavy metals in the beaches has been noticed due to the increase of human activities. This study aimed to evaluate heavy metal pollution, its ecological risk, and possible sources in the coastline of Dayer Port, Bushehr province.

Methods: The sediment samples were collected from 8 stations with different uses in 0-5 and 5-20 cm depths. The samples were evaluated to measure the concentration of Pb, Cu, Ni, and Mn after acid digestion by atomic absorption spectrometry (AAS). Subsequently, the ecological risk index was used to evaluate the environmental risk potential caused by heavy metal pollution. The statistical analysis was used to determine the source of pollutants and their relationship.

Results: The average concentration of Mn, Ni, Cu, and Pb were 218.59, 10.44, 11.78, and 7.81 µg g^{-1} in surface sediments and 278.05, 15.79, 12.74, and 10. 75 µg g^{-1} in deep sediments, respectively. The results of evaluating the ecological risk index caused by heavy metal pollution in the coastal sediments of the studied area showed that the environmental risk is low (>150). The results of multivariate statistical analyses showed that the investigated metals are of natural and anthropogenic origin mainly natural sources.

Conclusion: The presence of heavy metals in all collected sediment samples shows that heavy metals are common pollutants in the study area. As a result, regular monitoring of the area is important to control and reduce heavy metal pollution.

Keywords: Heavy metals, Environmental pollution, Human activities

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Introduction

The coastal zone is a key zone that connects land and sea. These areas are sensitive and vulnerable due to the interaction of land and sea and pollution caused by human activities (1). In recent years, coastal areas have been exposed to various types of pollution due to the rapid social and economic development and the direct and indirect discharge of a large number of pollutants (2-4). Heavy metal pollution in coastal sediments is one of the important indicators of environmental quality that can be used to show the state of pollution and ecological risk assessment (5). Unlike organic compounds, heavy metals do not decompose through chemical and biological processes in nature and are stable pollutants (6). Some heavy metals play an important role in the life and survival of living organisms, and many heavy metals are important components of the geochemical elements of soil and sediment, whose distribution is influenced by sediment characteristics and human activities. However, the increase in the concentration of these metals for various reasons causes the disturbance of the ecological balance and the biological destruction of the ecosystem (7). Heavy metals can be released into the ocean by natural factors such as surface runoff and atmospheric sedimentation and anthropogenic factors such as direct discharge as a result of human activities (5). In some conditions, heavy metals in seawater can interact with suspended particles through absorption, complexation, and sedimentation, and are transferred to the surface sediment (1,8,9). Heavy metals in sediments may be released into seawater by changing environmental parameters (e.g., pH, dissolved oxygen, and salinity) and cause secondary pollution of seawater. Therefore, sediments are not only carriers of pollutants but also the source of pollutants (1-5). Heavy metals introduced into coastal environments can directly affect the physical and chemical properties of sediments and inhibit microbial activities (7). In addition, heavy metals are accumulated in aquatic environments by plants, animals, and other living organisms, and are even magnified through the food chain (10-13). Therefore, sediments and water are widely used to monitor heavy metal pollution in coastal areas (1). Since heavy metals remain in the environment for a long time and accumulate in the body of living organisms, and also, due to their high toxicity, accumulation, and poor biodegradability, they can seriously endanger the health of marine animals, humans, and the natural environment (1,5,6). As a result, determining the concentration of heavy metals in coastal sediments and their potential environmental risks is very important for the management and protection of coasts. In addition, determining the concentration of heavy metals helps to better understand the relationships between development, exploitation, and protection of the coastal environment (4,5).

Since almost 99% of the heavy metals that enter the water systems are stored in the surface sediments of the beaches (4), many studies have been done to investigate and identify the concentration of heavy metals in different beaches by Rezaei et al (14), Delshab et al (15), Arfaeinia et al (3), Saadati et al (16), Liu et al (5), and Shu et al (4). Considering that the oil, gas, and petrochemical industries on the Persian Gulf coasts, which drive Iran's economy as well as various human activities such as maritime transport industries, aquaculture farms, and urban and industrial wastewater are among the main sources of heavy metal runoff on these beaches, more studies on the identification of metal pollutants in this area can be useful in applying control approaches to protect the ecosystem (9,17). In addition, the ecological risk assessment of heavy metal levels in coastal ecosystems is very important due to their potential toxicity, stability, bioaccumulation tendency, and general concern for the safety of seafood (10). This study was carried out to evaluate the concentration and ecological risk of heavy metals (Cu, Ni, Pb, and Mn) in the surface and deep sediments of the beaches of Dayer Port in Bushehr province in January 2019.

Materials and Methods

The study area

The Persian Gulf is a semi-enclosed border sea with minimal water exchange and an average depth of 35-40 m, which is affected by the dry and semi-tropical climate. The Persian Gulf is considered one of the areas affected by human activities in the world. Stressful environmental conditions such as extreme heat (>30°C) in summer and cold (<10°C) in winter, shallow depth, limited circulation, high evaporation and salinity, and low annual rainfall have caused the existing pollutants for a long time in this area. Therefore, the impact of pollutants in the region on the marine environment can be significant (10). Dayer Port, with a population of 24 084 people, is located in the south of Bushehr province and on the coast of the Persian Gulf. This port is known as the largest fishing port in Iran with a 95 km long sea border strip, hot and humid climate, and average annual rainfall of 215 mm, and its coast is one of the most beautiful places around the area. Figure 1 and Table 1 show the location of the studied area and the geographical coordinates of 8 sampling stations (D_1- D_8). Sampling stations were selected based on the type of area and exposure to pollution from different sources (e.g., areas D_1-D_4 residential areas and areas D_5-D_8 fishing areas) as well as their availability for sampling.

Sampling and preparation of sediment samples

To determine the concentration of heavy metals, sediment samples were collected in January 2019 from 8 stations in the low tide line of the Persian Gulf coast in a transect with a length of 1000 m using quadrats of 30×30 cm^2, in three repetitions and two depths of 0-5 and 5-20 cm. The sediment samples were taken from each station using a pre-cleaned stainless-steel shovel and a metal ruler at two depths. The wet weight of each sediment sample was about 2 kg. Then, the samples were transferred to the laboratory in numbered plastic bags. All sediment samples were dried in an oven at 60 °C for 24 hours and powdered. Powdering sediment samples is often done due to the presence of heavy metals with small grains (18). The powdered samples were sieved through a stainless-steel sieve with mesh No. 100 (sieve hole size: 0.150 mm), and stored in clean plastic bags for further analyses.

Acid digestion of sediment samples

The plastic and glass containers used for digestion and measurement of heavy metal concentration were immersed in an acidic washing solution (10% nitric acid) for 24 hours, and then, washed with distilled water and dried in an oven. To perform the digestion operation, a sample composed of three replicates of each station was separated and homogenized. Then, 1 g of homogenized sediments was digested in PTFE tubes using a mixture containing 7 mL HNO_3, 5 mL $HCLO_4$, and 2 mL HF at 200 °C for 8 hours. After cooling, the samples were filtered through a Whatman 42 µm filter paper, and the extracted solution was diluted with distilled water to 25 cc. The diluted samples were stored in special plastic containers after centrifugation at 400 rpm for 6 minutes. Finally, the concentration of heavy metals such as Ni, Pb, Mn, and Cu were measured by the flame atomic absorption spectrometer (AAS) GBC model. The results were validated by electrothermal atomic absorption spectrometry (GBC, Pal 3000, ET-AAS). The details of the instrument and reagents were presented elsewhere (19). In addition, the recovery test was performed to check the accuracy by preparing the stock solutions from the pure substance of each element. The standard solutions (1000 mg L^{-1}) from CHEM-LAB Belgium brand were used at

Figure 1. Location of the study area and sampling stations

Table 1. Geographical coordinates of sampling points

Station Name	Station Location	Geographical Coordinates	
		X	Y
D_1		594789	3079680
D_2		593931	3079564
D_3		593545	3079480
D_4	Dayer Port	587102	3079641
D_5		582212	3080134
D_6		580369	3080112
D_7		579285	3079898
D_8		578642	3079725

five concentrations of 0, 1.5, 2, 3.5, and 5 mg/L for Pb, four concentrations of 0, 1, 1.5, and 2.5 mg/L for Cu, three concentrations of 0.2, 1.4, and 2.4 mg/L for Ni, and four concentrations of 0, 1, 2, and 4 mg/L for Mn to implement the concentration-absorption curve of each element. The estimation of recovery for each element was 99.1%, 99.4%, 99.9%, and 99.8% for Pb, Cu, Ni, and Mn, respectively. The limit of detection (LOD) was 0.06 µg mL^{-1} for Pb, 0.025 µg mL^{-1} for Cu, 0.04 µg mL^{-1} for Ni, and 0.02 µg mL^{-1} for Mn.

Ecological risk assessment

The potential ecological risk index (RI) was used to evaluate the level of pollution and the potential ecological risk of heavy metals in the coastal sediments of the study area according to the toxicity, response of the environment, and using the information related to the ecology of the area. The relationship for calculating potential ecological risk and the equations used to calculate RI were proposed by Hakanson (20) as follows:

$$RI = \sum_{i=1}^{n} Er = Tr \times Cf = Cs / Cb \quad (1)$$

In this equation, *RI* represents the potential ecological risk caused by the pollution of all metals (cumulative), *Er* is the potential ecological risk of each heavy metal, *CF* is the contamination index of heavy metal, *Cs* is the measured concentration of the heavy metal in the sample, *Cb* is the concentration of the same heavy metal in the background (concentration of the element in shale), and *Tr* is the toxic response factor that reflects the level of ecological risk of the investigated heavy metals. Toxic response factor values for Pb, Cu, Ni, and Mn are 5, 5, 5, and 1, respectively (15). In this study, the average shale presented by Turekian and Wedepohl (21) was used as the background concentration to determine the amount of sediment contamination with heavy metals (Table 2). The classification of the ecological risk status of the studied heavy metals is shown in Table 3.

Statistical analysis

In this study, statistical analyses were performed using SPSS statistical software version 22. The normality of the data was evaluated by the Kolmogorov-Smirnov test. Then, independent two-sample mean tests were used to understand the changes in the concentration of heavy metals at two depths of 0-5 and 5-20 cm. In addition, principal component and cluster analysis were used to explain the pattern of correlation between heavy metals,

Table 2. Concentration of heavy metals in average shale (ppm)

Metals	Pb	Cu	Ni	Mn
Average	20	45	68	850

Table 3. Classification of ecological risk based on Er (20)

Risk levels description	Category	Risk levels description	Category
Low risk	RI≤150	Low risk	Er≤40
Moderate risk	150≥ RI≥300	Moderate risk	40≥Er≥80
Considerable risk	300≥ RI≥600	Considerable risk	80≥Er≥160
High ecological risk	RI ≤600	High ecological risk	160≥ Er≥320
-	-	Very high risk	Er≤ 320

identify possible sources, and group them based on similarities and differences. Also, Pearson's correlation test was used to find the correlation between heavy metals in the studied area. In addition, a significance level of 5% (95% confidence level) was considered for all statistical tests.

Table 4. Descriptive statistics of heavy metal concentrations (µg g^{-1}) in surface and deep sediments of eight sampling stations

Sampling depth	Descriptive statistics	Heavy metals			
		Mn	Ni	Cu	Pb
Deep sediments	Minimum	203.40	10.00	11.00	0.00
	Maximum	358.00	25.02	15.47	48.60
	Average	278.05	15.79	12.74	10.75
	Standard deviation	52.21	4.78	1.60	16.11
	Coefficient of variation	0.18	0.30	0.12	1.49
	Skewness	-0.08	1.15	0.64	2.31
	Kurtosis	-0.71	1.03	-0.82	5.70
Surface sediments	Minimum	157.42	4.97	9.82	1.80
	Maximum	357.70	17.20	14.35	14.95
	Average	218.59	10.44	11.78	7.81
	Standard deviation	61.75	3.90	1.40	5.47
	Coefficient of variation	0.28	0.37	0.11	0.70
	Skewness	1.86	0.30	0.67	0.17
	Kurtosis	4.44	0.07	0.49	-2.02

Results

The results of the measurement of heavy metal concentration in the surface and deep sediments of eight sampling stations in Dayer port are presented in Table 4. Mn and Pb with concentrations of 218.59 ± 61.76 and 7.81 ± 5.47 (µg g^{-1}) dry weight of surface sediment and 278.05 ± 52.21 and 10.75 ± 16.11 (µg g^{-1}) dry weight of deep sediment had the highest and lowest average concentrations among the studied metals in surface and deep sediments, respectively. Pb and Cu with the coefficient of variation (CV) of 0.7 and 0.1 had the highest and lowest CV among the studied heavy metals in the surface sediments of the study area, respectively. Also, Pb and Cu with CVs of 1.49 and 0.12 had the highest and lowest CV in deep sediments, respectively. A CV higher than 1 indicates high variability and non-uniform distribution, and a CV lower than 1 indicates low variability of the studied heavy metal in sediment (4). In this study, only Pb in deep sediments had a CV higher than 1. The CV shows that heavy metals in sediments are dispersed on average under the influence of environmental conditions, and human activities have helped increase their concentration. Also, the results of comparing the concentration of Cu, Mn, Ni, and Pb in surface and deep sediments of the coasts of Dayer port showed that there was no significant difference between the average concentration of Cu, Pb, and Mn in two depths ($P > 0.05$). In contrast, the concentration of Ni in deep sediments was significantly higher than in surface sediments ($P < 0.05$).

Correlation analysis and determination of the sources of heavy metals

The results of Pearson's correlation coefficient of the investigated heavy metals are presented in Table 5. Accordingly, in the sediment samples, there was a moderate and positive correlation between Pb and Ni, and Ni and Mn at the level of 1% ($P < 0.05$). Also, the results of the principal component analysis, which was carried out to identify possible sources of heavy metals in sediments, are presented in Table 6. Based on the results of this analysis, the variables were divided into two main components, which included 81.19% of the total variance. The first component covered 54.05% of the total variance and presented a positive loading for Pb, Mn, and Ni, while the second component covered 27.14% of the total variance and showed a positive loading for Cu. In addition, heavy metals were classified into two statistically significant clusters based on the cluster analysis (Figure 2). The first cluster included Pb, Ni, and Mn, which indicates the same origin of these metals and the second cluster included Cu metal. The results of the cluster analysis almost confirm the results of the correlation analysis and principal component analysis.

Ecological risk assessment

The individual ecological risk index of the investigated heavy metals in the surface and deep sediments showed the decreasing order of Pb > Cu > Ni > Mn. Also, the results of the ecological risk assessment of heavy metals in the surface and deep sediments of the studied stations were lower than 150, which indicates the low ecological risk of heavy metals in these areas.

Discussion

The identification of heavy metals in the sediment samples showed that they are the common pollutants in the study area. The reviews show that the coasts of the Persian Gulf

Table 5. Pearson's correlation coefficient of the studied heavy metals

Heavy Metal	Pb	Cu	Ni	Mn
Pb	1			
Cu	0.149	1		
Ni	0.643**	0.158	1	
Mn	0.425	0.122	0.664**	1

** Significance at the level of 0.01.

Table 6. The factor matrix and the periodic factor matrix of the investigated heavy metals

Heavy metal	Factor matrix		Periodic factor matrix	
	First factor	Second factor	First factor	Second factor
Pb	0.814	0.148	0.796	0.225
Cu	0.144	0.958	0.052	0.967
Ni	0.920	0.039	0.912	0.126
Mn	0.802	0.367	0.833	0.289

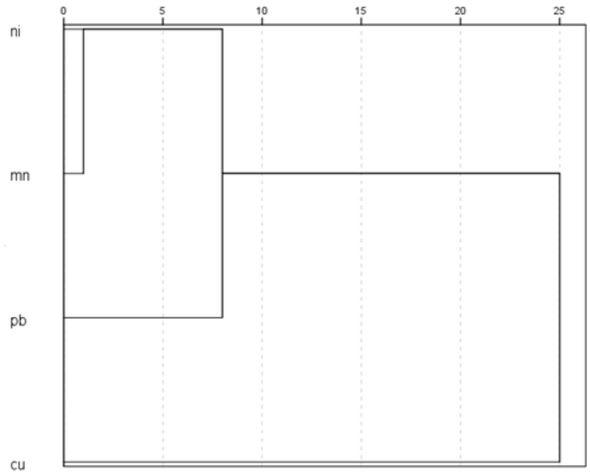

Figure 2. The results of heavy metals cluster analysis in the coastal sediments

are affected by oil pollution and its related industries, the activity of ships, and the entry of sewage. The largest number of oil and gas extraction and processing facilities are located in the Persian Gulf region. Therefore, the oil industry is one of the biggest threats to the marine and coastal environments of this region (22). As a result, regular monitoring of the area is very important to reduce pollution, especially heavy metal pollution.

In this study, the highest concentrations of heavy metals in surface sediments include Mn, Cu, Ni, and Pb, respectively, and in deep sediments include Mn, Ni, Cu, and Pb, respectively. The concentration of Ni and Cu in this study was higher than Pb, which was similarly presented by other studies in the Persian Gulf (15,23). However, the results of the study by Arfaeinia et al (3) in the same area showed that the concentration of Pb was higher than that of Ni and Cu. Arfaeinia et al (3) in their study on the Persian Gulf beaches of Bushehr province with industrial use showed that the concentration of most pollutants is much higher than in other beaches of Bushehr province. The high concentration of heavy metals in industrial and commercial areas compared to non-industrial areas shows that human activities have a greater impact on the concentration and distribution of heavy metals in the environment than other factors. In these areas, industrial and urban sewage, agricultural and aquaculture effluents, waste disposal, fishery and commercial cargo boats, and atmospheric depositions are of the most important factors in increasing the concentration of heavy metals and reducing the biodiversity in sediments (22). Due to the population distribution and industrial activities, atmospheric depositions can affect large areas (1). Weathering, river bank erosion, and washing soils containing fertilizers and agricultural toxins by floods are other possible sources of sediment pollution and, as a result, the accumulation of heavy metals on the coasts (9,24). Predicting the toxic effects of heavy metals in sediments is greatly significant due to the interaction of heavy metals with the biological macromolecules and the possibility of disrupting their physiological and metabolic functions and following that poisoning and even the death of organisms (5). The results of comparing the heavy metals concentration in the studied beaches showed the difference in the concentrations among the beaches. The concentrations of heavy metals in sediments are influenced by many factors such as sediment texture and mineralogical composition, physical and chemical properties of sediment such as pH and temperature, biological effects and human activities, the number and type of pollution sources in the environment, and the distance from the pollution source to the sampling site (5).

The main reason for the change in the concentrations of heavy metals in each region is related to the type of industry, the amount of their wastewater output, and the amount of heavy metals in the environment (14). The presence of heavy metals in the sampling stations is probably due to the proximity to the city of Dayer Port, the oil platform, the passage of oil tankers and the petrochemical complex, commercial and fishing boats, the discharge of municipal and industrial wastewater, and the tourism activities in the area. Therefore, human activities and the location of pollutants discharged resulting from these activities are important reasons for the geographical distribution of heavy metal pollution in the environment (10).

In this study, stations D7 and D8 showed the highest concentration of heavy metals in surface and deep sediments, respectively. These two stations are located near the tourist beaches and fishing port with high fishing activities and boat traffic. The use of river water that may have been contaminated by urban and industrial wastewater discharge can be another reason for the heavy metal pollution in the region. Rivers polluted with industrial and domestic wastewater significantly increase the concentration of various pollutants such as heavy metals, microplastics, Polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) in beach sediments (1).

In the results of the principal component analysis, which was done to identify possible sources of heavy metals in the sediments, the second component presented only positive loading for Cu. Also, the correlation of Cu with other heavy metals was low, indicating that the source and entry routes of this heavy metal are significantly different from Ni, Mn, and Pb, and are mainly influenced by human activities. Cu metal is widely used due to its special physical characteristics, so the presence of Cu is probably the result of industrial activities in the investigated beaches (24). In this study, the highest concentration of Cu was detected near the construction site of metal floats and residential areas with agricultural and aquaculture activities. As a result of the discharge of urban sewage, agricultural pesticides, and aquatic feed (as an essential and promoter element) on the beach, as well as transit of vehicles, ships, and boats in the water environment, and the release of the paint used in them can be among the ways of the entering of Cu in the beach sediments (10). Cu can become toxic to organisms' lives at higher levels than the threshold limits, while Cu is a micronutrient for organisms in all aquatic environments at low concentrations (25). In the cluster analysis, Pb, Ni, and Mn were placed in one cluster. Therefore, it can be concluded that these metals have similar geochemical characteristics, and therefore, probably originate from the same sources. Since Mn is a major chemical component of marine sediments, it reflects the influence of sediment geochemical composition on pollutant concentrations (4). The use of agricultural pesticides and fertilizers, the discharge of industrial wastewater, and the use of diesel fuel in commercial cargo boats may increase the concentration of Mn in coastal sediments (26). The results of multivariate statistical analysis clearly showed the existence of a common origin and correlation between Ni and Mn. The high concentration of Ni and Mn in the sediments of station D8 indicates the existence of the same sources of origin and the similar behavior of these two heavy metals. The presence of Ni in the region is probably caused by land resources including clay, basalt, and sandstone minerals, human activities related to petroleum products and paints used in industry, machinery, and ships (1,16,24).

The concentration of Pb in nature is low, so human activities increase Pb concentration in the environment (8). Among the studied stations, stations D_2 and D_8 showed the highest concentration of Pb in surface and deep sediments, respectively. These two stations were located near the residential area and fishing port. Therefore, unusual concentrations of Pb may be related to the excessive recreational activities at the beach, proximity to roads and road transport, fishing vessels activity, and release of paint from ship hull (10). Lead is widely used in antifouling paints to enable corrosion resistance. Therefore, the antifouling paints used on the coating and propeller of fishing vessels may contribute to Pb in sediment pollution (9,10). Atmospheric deposition containing polluted gases released from industrial stacks and vehicle exhausts is another source of Pb in the environment. As a result, it can be concluded that the ships' transportation and automobile exhausts contribute greatly to the concentration of Pb in sediment (1). In general, the population increase, urban development, and the increasing activities related to the oil industry pose a serious threat to the ecosystem of the Persian Gulf coast. One of the main effects of urbanization and industrialization on marine ecosystems is the loss of sensitive species and the reduction of biodiversity (22). The ecological risk assessment index in the area was less than 150, indicating that the situation of sediment pollution in the region related to the investigated heavy metals is not in a dangerous and critical state.

More precision in the analyses and results was not possible due to the number of sampling points. Finding out the pattern of spatial distribution of heavy metals in surface sediments can be the basis of appropriate action for the protection of marine sediments, which is one of the limitations observed in the present research. Also, it was not possible to compare the data of this study with other studies in the same region due to the lack of more studies. In addition, due to the presence of various industries in the region and the toxic properties of the metals for living organisms and even humans, it is necessary to measure other heavy metals such as cadmium, zinc, and mercury in addition to the examined heavy metals.

Conclusion

Coastal ecosystems in all parts of the world have been influenced by anthropogenic pressure and habitat degradation, and the Persian Gulf is no exception. In the present study, the pollution status, spatial distribution, and possible sources of heavy metals pollution in the surface and deep sediments of the Persian Gulf coast in Dayer Port of Bushehr province were investigated. The study of pollutants concentrations in two depths has rarely been discussed in previous studies, however, the study of other heavy metals concentrations in the area may be considered in future studies. The results of this study indicated that heavy metals in the sediments of the studied area moderately disturbed by environmental conditions and human activity had contributed to their enrichment. The concentration of investigated heavy metals in the surface and deep sediments showed the decreasing order as Mn > Cu > Ni > Pb and Mn > Ni > Cu > Pb, respectively. There was no significant difference between the average concentration of Cu, Pb, and Mn in the two depths ($P > 0.05$). In contrast, the concentration of Ni in deep sediments was significantly higher than in surface sediments ($P < 0.05$). The observations indicated that there was a positive correlation between Pb and Ni as well as Ni and Mn ($P < 0.05$). So, with the increase in the concentration of Ni, the concentration of Pb and Mn also increases. The results of multivariate statistical analyses have also confirmed the existence of this relationship. Finally, according to the ecological risk assessment index, the situation of sediment pollution in the region related to the investigated heavy metals is not in a dangerous and critical state. However, due to the increase in population growth, urbanization, and industrialization, it is expected that the coastal living and non-living resources will continue to be under increasing pressure. Therefore, a comprehensive management plan is needed to protect coastal resources in the future.

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Competing interests
The authors declare that they have no conflict of interests.

Ethical issues
The authors certify that all data collected during the study are as stated in the manuscript, and no data from the study has been or will be published elsewhere separately.

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