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Multivariate Analyses to Determine the Origin of Potentially Harmful Heavy Metals in Beach and Dune Sediments from Kizkalesi Coast (Mersin), Turkey

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Abstract The aim of this study was to investigate variations in heavy metal concentrations and natural and artificial sources of heavy minerals in beach and dune sediments along Kizkalesi (Mersin) coast in Turkey. To this aim, sand sediment samples were collected from 20 locations throughout Kizkalesi coast and concentrations of Zn, Ni, Cu, Co, V, Mo, Ag, Sb, Sn, Cd, W, Hg, Pb, As, Si, Al, Fe, Ca, Mg, S, K, Na, Cl, Ti, Mn and Cr were determined. Simple analyses (frequency histogram), multivariate analyses (Coefficient correlation, Cluster Analysis), Principal Component Analysis, Model Summary and ANOVA were used to analyze the concentration values. Al, Fe, Mg, Cl, Ti, Mn, Cr and Ni were dominant heavy metals. Principal Component Analysis revealed six principal components. It was confirmed by Cluster Analysis. Based on the Hierarchical Cluster analyses, three different general groups were formed at a 50% arbitrary similarity of Q-type level. The frequency histogram indicated that W, Ag, Co, V, Cu, As, Sn, Ni, Zn, Pb, Cr, Cl and Mg concentrations originated from the nearby area, while Mn, Ti, Al and Fe Mg concentrations came from either the nearby area or moderately remote sources. Data from the study area showed that the Model Summary (based on $R^2 = 100\%$) was sufficient for the statistical data and that the Model ANOVA (variations of Pb) had a high explanatory power. The region lying on Miocene carbonate rocks of the Tauride belt were affected by the contaminants of anthropogenic origin that included coastal deposits, coastal erosion, the Kizkalesi settlement area, urban wastes, Mersin-Antalya road extending parallel to the shoreline and disposal sites of hotels.

Keywords Heavy metals · Multivariate analysis · Dune sediments · Kizkalesi · Mersin

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Soils (sediments) are environmental contaminants for rock, air and water interfaces. Soils are influenced by contaminants of different origin triggered by anthropogenic activities. Therefore, it is important to determine heavy metal concentrations and to investigate their geochemical distribution. There have been several recent studies on distribution of heavy metals along coastal areas (Evans 1971; Scoullos and Dassenakis 1982; Duan 2000; Wolf et al. 2001; Araujo et al. 2002; Rocha et al. 2005; Abrantes et al. 2005; Vidinha et al. 2006; Ramirez et al. 2005). To explain the differences between geogenic and anthropogenic sources of heavy metals, some methods have been developed. The most common one is the multivariate statistical methods (Facchinelli et al. 2001; Boruvka et al. 2005; Huang et al. 2007; Yalcin et al. 2007).

Mediterranean marine sediments are well known to be contaminated by heavy metals (Mulsow et al. 2001; Rouibah 2001; Yoshida et al. 2004). In the vicinity of the study area several environmental studies on biogeochemistry (Yilmaz 2002), soil parameters (Everest and Seyhan 2006), stratigraphy and seismic stratigraphy (Okyar 1991; Okyar et al. 2005), marine geological and geophysical composition (Ergin et al. 1989; Ergin et al. 2007), saltwater intrusion into a coastal aquifer in Mersin (Demirel 2004), urbanization and tourism on coastal environment (Burak et al. 2004), upper slope sediment waves in the Cilician Basin and north-eastern Mediterranean (Ediger et al. 2002) and dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin (Kocak et al. 2005) have been conducted. However, beach and dune sediments of Kizkalesi along the Mediterranean coast have not been studied before. In this respect, it is of great importance to investigate heavy metal contents in the sediments of Kizkalesi coast.

In the present study, heavy metal contents of beach and dune sediments in the Kizkalesi coast between Erdemli and Susanoglu were investigated. Considering the lithologic and geochemical characteristics, variations as well as anthropogenic and geogenic sources of heavy metal contents of beach and dune sediments in the southern part of the Miocene carbonate rocks of the Tauride belt were determined.

Materials and Methods

Situated (on a 1/100.000 scaled K34 Kayseri map) between Silifke and Erdemli towns, which were the heart of commerce in the triangle between Egypt, Cyprus and Roma, Kizkalesi was established in the antic Korykos city (called Safran in Turkish). Coordinates for the area were 38°20′ north and 35°16′ east and the altitude is 1,074 m. The historically important Korykos castle was located on the coast. The area was named after a castle built on a small island just across the area and still in good shape. The Kizkalesi area was attractive with its bright and clean seawater and a long beach extending along the coast. The study area was accessible through Mersin-Antalya road of 55 km from 35 km away from Erdemli exit (Fig. 1).

The Mesozoic lithological associations of Anatolia documented the development of a mosaic of microcontinents and carbonate platforms, separated by ophiolitic suture zones; the latter represented an oceanic crust formed as a result of the Triassic break-up of Gondwanaland (Ozer et al. 2004). This complex structure formed as a result of the closure of different branches of the multi-branched Neo-Tethys Ocean during the Late Cretaceous−Miocene (Sengor and Yilmaz 1981; Sengor 1987) (Fig. 1). The study area was located in the southern part of Miocene carbonate rocks of the Tauride belt. Depositional environments of the sedimentary rocks in the central Tauride belt were described as a "unit" (Ozgul 1971, 1976). Formations in the region were deposited in terrestrial conditions at the beginning of Miocene and then in marine conditions in the following periods. During the deposition, lithology was dependent on an old topography and units were not significantly disturbed (Gedik et al. 1979).

Sand sampling along the coast was conducted in August, 2006 and 20 systematic samples were collected from a depth of 0–10 cm (Fig. 1). Coordinates for sampling sites were determined with Garmin brand GPS-12CX device and they were marked on a 1/100.000 scaled topographic map. Samples were collected with a hard plastic sample shovel and stored in 1-kg plastic bags.

In order to minimize the contamination, bags were washed with 6 M HNO_3 and rinsed with distilled water and then heated at 70°C before they were used. Soil samples

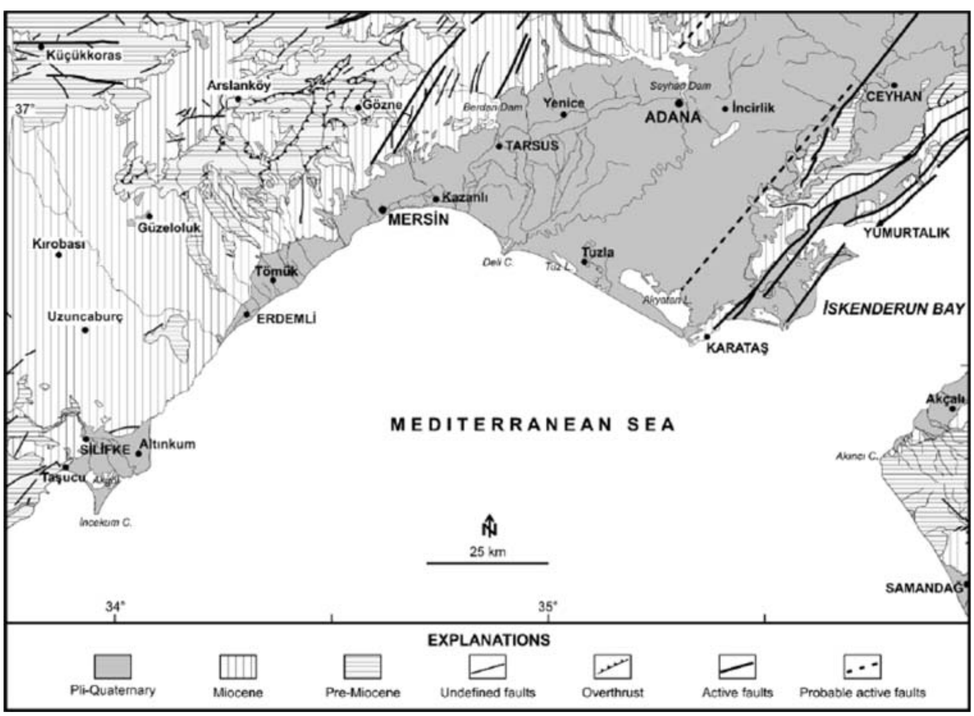

Fig. 1 The Tethyside tectonic units of Turkey (after Sengor 1987) and the areas of the present study (MTA 2002)

were heated at 105°C for 24 h. Dried samples were sieved through a 2 mm plastic sieve to remove conglomerates. In the next stage, the samples were homogenized with an agate mortar to a grain size of less than 2 mm. The mortar was washed with 6 mol L^{-1} HNO_3 and rinsed with distilled water and dried before each sample process.

Analyses of Sb, W, Ag, Mo, Co, V, Cu, As, Sn, Hg, Ni, Zn, Cd, Pb, Si, Al, Fe, Ca, Mg, S, Na, K, Cl, Ti, Cr and Mn contents were performed with Spectro-Xepos Benchtop X-Ray Fluorescence Spectrometer. Prior to analyses, all the samples were transformed to double-sided film tablets with a diameter of 32 mm. The detection system was a microprocessor controlled drift detector with Peltier cooling and energy resolution of FWHM <170 eV, measured for the Mn Kα line with an input count vote of 10.000 pulses. Results were expressed in mg/kg.

It is very important to determine statistical behavior of heavy metal contents in beach sediments of the Kizkalesi area. Identification of heavy metal groups and their interrelations are important factors for a source evaluation (Davis 1986). Since there were partial differences in the vertical column at the sampling sites, there explanation required some geochemical interpretation (Fachinelli et al. 2001). Raw data from chemical analyses were stored in MS Excell program. For the geochemical interpretations, priority was given to simple statistical processes. In order to reveal all characteristics of the study area, the data were analyzed with simple statistical tests. In addition, variations in heavy metal contents and their interrelations were evaluated with SPSS software for multivariate statistical analyses (Coefficient correlation, Cluster Analysis, Principal Component Analysis, Model Summary and ANOVA). Their maps were drawn with Arc View.

Results and Discussion

Minimum concentrations of the heavy metals Zn, Ni, Cu, Co, V, Mo, Ag, Sb, Sn, Cd, W, Hg, Pb, As, Al, Fe, Mg, Cl, Ti, Mn and Cr were 12.9, 117.3, 6.2, 2.2, 40.6, 2.5, 3.1, 5.5, 7, 3.7, 6.8, 1.5, 3, 20.1, 4971, 10850, 23400, 803, 448.2, 467 and 325, respectively, and maximum concentrations of the heavy metals Zn, Ni, Cu, Co, V, Mo, Ag, Sb, Sn, Cd, W, Hg, Pb, As, Al, Fe, Mg, Cl, Ti, Mn and Cr were 30.4, 374.5, 14.5, 39.1, 121, 35, 6, 6.4, 9, 4.7, 9.2, 3.2, 5.9, 32.5, 12870, 31060, 62490, 14100, 1607, 857 and 889, respectively.

Results of chemical analyses of the samples collected from Kizkalesi coast are shown in Table 1. Results of analyses of the chemical data (Zn, Ni, Cu, Co, V, Mo, Ag, Sb, Sn, Cd, W, Hg, Pb, As, Al, Fe, Mg, Cl, Ti, Mn, Cr) with simple statistical techniques are shown in Table 2.

Variations of heavy metal contents based on statistical analyses are illustrated in Fig. 2. There were differences between variations of heavy metal contents. In comparison to other metals, Al, Fe, Mg and Cl in the area had the highest concentrations, followed by Ti, Mn, Cr and Ni. V, Co, Mo, Zn, As and Cu had moderate concentrations, while Sn, Ag, W, Hg, Pb, Sb and Cd had minimal concentrations. Frequency histograms of each element revealed that W, Ag, Co, V, Cu, As, Sn, Ni, Zn, Pb, Cr, Cl and Mg elements were generally condensed on the first parts of the histogram. However, Mn, Ti, Al and Fe were found in the first and central parts, while Cd, Mo and Hg were observed in the central part of the histogram (Fig. 3). There have been several heavy metal studies conducted on beach and dune sediments in various regions (Turekian and Wedepohl 1961; Vidinha et al. 2006). Comparisons of average heavy metal contents from the study area with those from Portugal dune sediments revealed some differences (Table 3). The average concentrations of heavy metals in soils were generally lower than those of Portugal dune sediments. However, Ni, Mg, Mn and Cr contents of Kizkalesi coast dune sediments were higher. These differences can be attributed to regional differences in both areas.

Considering heavy metal contents of the earth crust (Krauskopf 1979), heavy metal contents of the study area were considered abnormal. Hg had the highest concentration followed by Ag, Cl, Sb, Cd, Mo, As, W, Cr, Sn, Ni, Mg, Co and Cu. Based on the heavy metal contents acceptable for Turkey, Cl had the highest concentration followed by Ni, Cr, Mo, Hg, Co and As. Since acceptable cut-off values of all heavy metals in Turkey were not available, we could not calculate abnormal concentrations of all metals. However, Cl, Ni, Cr, Mo, Hg, Co and As had abnormal concentrations based on acceptable cut-off values for both Turkey and the earth crust values. Therefore, they deserve attention.

According to the results of soil sample analyses and coefficient correlations between the metals, there was a *strong positive correlation* between **Zn** and V, Al, Fe, Ti, Mn and Cr; between **Ni** and W, As and Mg; between **Cu** and W and Al; between **Co** and Mo; between **V** and Al, Fe, Ti, Mn and Cr; between **W** and As and Mg; between **As** and Mg; between **Al** and Fe, Ti, Mn and Cr; between **Fe** and Mg, Ti, Mn and Cr; between **Ti** and Mn, Cr; between **Mn** and Cr. A *moderate positive relation* was found between **Zn** and Cu and Mg; between **Ni** and Cu and Fe; between **Cu** and Co, V, Fe, Mg, Ti, Mn and Cr; between and Sn, between **W** and Fe; between **As** and Cl; between **Al** and Mg; between **Mg** and Cl and Cr. There was a *moderate negative relation* between **Cu** and Ag; between **Co** and Ag; between **Ag** and Cd, W and As (Table 4).

Results of Principal component analysis (PCA) conducted on chemical analyses are supplied in Table 5. All elements were well represented by six principal components. Based on initial component matrix indicators, Fe, Al,

Table 1 Results of chemical analyses of samples from the study area

Samples	KKS-1	KKS-2	KKS-3	KKS-4	KKS-5	KKS-6	KKS-7	KKS-8	KKS-9	KKS-10	KKB-11	KKS-12	KKS-13	KKS-14	KKS-15	KKS-16	KKS-17	KKS-18	KKS-19	KKS-20
Zn	30.40	25.80	23.80	21.10	17.14	15.00	13.50	12.90	15.80	15.70	19.30	22.10	21.90	20.50	19.60	20.50	19.90	19.40	21.20	19.50
Ni	197.20	218.50	159.60	137.10	133.11	139.50	117.30	151.70	152.20	134.60	148.90	200.60	210.90	201.00	158.10	188.00	197.40	190.70	374.50	325.00
Cu	14.50	11.60	9.40	9.90	7.91	8.40	6.20	11.40	11.50	9.70	7.40	9.40	11.90	8.50	10.00	8.40	11.30	11.90	13.70	9.50
Co	32.10	32.40	26.30	38.50	26.77	25.00	22.70	30.00	20.00	36.70	2.20	32.00	28.00	24.10	30.00	25.90	33.10	35.20	39.10	24.00
V	121.00	80.00	93.00	69.90	58.27	41.70	45.50	40.60	47.80	57.10	64.40	70.20	59.30	64.20	52.00	49.70	68.20	52.10	67.30	63.70
Mo	28.00	25.00	26.00	27.00	26.63	26.00	27.00	35.00	28.00	25.00	2.50	35.00	27.00	25.00	25.00	26.00	26.00	29.00	25.00	25.00
Ag	4.40	3.70	4.80	4.10	4.93	3.40	6.00	3.90	5.00	3.90	4.80	3.80	3.70	3.60	3.40	5.10	3.10	3.70	3.60	3.70
Sb	5.50	6.30	5.90	5.90	6.04	5.70	6.30	5.80	6.00	5.80	5.90	6.40	6.20	5.80	6.30	5.70	5.90	5.70	5.80	6.00
Sn	7.00	8.40	7.80	7.90	7.78	7.10	8.00	8.20	8.60	8.40	7.70	9.00	8.30	8.50	8.50	8.80	8.80	8.20	8.20	8.20
Cd	3.90	4.30	4.20	4.50	4.04	4.20	3.70	4.10	4.10	4.40	4.10	4.40	4.30	4.40	3.90	4.30	4.70	4.20	4.50	4.00
W	7.70	8.00	7.30	7.50	7.21	7.30	7.00	7.40	7.50	7.00	6.80	7.80	7.80	7.60	7.40	7.60	7.90	7.50	9.20	8.70
Hg	2.20	2.00	2.10	1.50	2.08	2.10	2.30	2.00	1.50	1.60	2.00	2.10	2.10	1.50	2.20	1.90	3.00	3.20	2.00	1.70
Pb	4.20	4.40	4.90	5.10	4.52	4.30	4.20	5.20	5.90	4.00	3.80	5.10	3.40	3.90	5.50	4.10	5.20	3.00	5.40	4.90
As	20.10	24.70	22.00	23.40	21.89	23.30	20.60	22.20	22.80	23.80	22.10	26.60	26.20	26.00	24.90	25.70	24.90	29.30	31.90	32.50
Al	12850.00	12870.00	9235.00	8992.00	6693.38	5872.00	4971.00	5491.00	6357.00	6104.00	7271.00	8859.00	9809.00	8773.00	8545.00	8665.00	8708.00	8180.00	9763.00	7335.00
Fe	31060.00	27870.00	22940.00	20490.00	15162.50	12120.00	10850.00	11680.00	13360.00	14050.00	18650.00	18010.00	20310.00	21590.00	18610.00	18300.00	19260.00	18410.00	22050.00	21300.00
Mg	42120.00	42980.00	33110.00	29680.00	26870.63	25920.00	23400.00	24320.00	27100.00	26420.00	29850.00	32340.00	37170.00	35770.00	32660.00	34110.00	37960.00	39660.00	55930.00	62490.00
Cl	7184.00	803.00	10150.00	3332.00	4751.31	1839.00	4294.00	6365.00	5996.00	5990.00	8144.00	7685.00	8865.00	7811.00	7051.00	6972.00	6629.00	8550.00	6190.00	14100.00
Ti	1607.00	1348.00	1100.00	924.00	672.83	518.60	448.20	492.00	577.00	547.00	754.00	853.00	954.00	865.00	833.00	825.00	813.00	756.00	791.00	591.00
Mn	857.00	781.00	666.00	643.00	537.88	470.00	467.00	479.00	528.00	482.00	552.00	652.00	609.00	610.00	572.00	597.00	606.00	553.00	554.00	504.00
Cr	869.00	889.00	760.00	557.00	514.75	355.00	460.00	325.00	402.00	465.00	445.00	534.00	644.00	432.00	518.00	479.00	678.00	503.00	627.00	620.00

Table 2 Results of simple statistical parameters computed from the chemical data

	Zn	Ni	Cu	Co	V	Mo	Ag	Sb	Sn	Cd	W	Hg	Pb	As	Al	Fe	Mg	Cl	Ti	Mn	Cr
N	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Mean	19.752	186.7955	10.1255	28.2035	63.2985	25.9565	4.1315	5.947	8.169	4.212	7.6105	2.054	4.551	24.7445	8267.169	18803.63	34993.03	6635.066	813.4815	585.994	553.8375
Minimum	12.9	117.3	6.2	2.2	40.6	2.5	3.1	5.5	7	3.7	6.8	1.5	3	20.1	4971	10850	23400	803	448.2	467	325
Maximum	30.4	374.5	14.5	39.1	121	35	6	6.4	9	4.7	9.2	3.2	5.9	32.5	12870	31060	62490	14100	1607	857	889
Std. deviation	4.16388	63.70973	2.09402	8.12111	18.751	6.24335	0.74159	0.24446	0.51998	0.24091	0.55772	0.43577	0.75003	3.37691	2131.019	5153.68	10127.71	2902.99	286.6746	100.7466	155.1207
Skewness	0.571	1.869	0.272	−1.621	1.657	−2.735	0.954	0.379	−0.749	−0.116	1.44	1.216	−0.199	1.026	0.658	0.537	1.434	0.285	1.306	1.245	0.821
Std. error of Kurtosis	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992	0.992

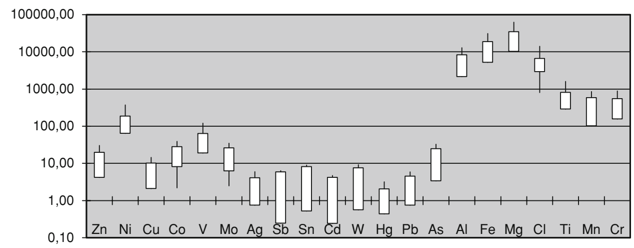

Fig. 2 Heavy metal concentrations in beach and dune sediments of Kizkalesi coast

Zn, Cr, Ti, Mn and V with high value indicators were found together within the first component. The first factor (Factor 1) explained 37.74% of the total variance with a high eigenvalue of 7.925. This factor can be termed as "*anthropogenic factor*". The second factor (Factor 2) explained 18.762% of the total variance with an eigenvalue of 3.940 and high values of Mg, As, W, Ni and Cl. This factor can be termed as "*natural process factor*". They were associated with the calcareous materials. The third factor (Factor 3) explained 10.529% of the total variance with an eigenvalue of 2.211 and high Cu, Mo, Co and Pb values. The fourth factor (Factor 4) explained 7.583% of the total variance with an eigenvalue of 1.593 and a high Cd value. The fifth factor (Factor 5) explained 6.027% of the total variance with an eigenvalue of 1.266 and high values of Sn and Sb. The sixth factor (Factor 6) explained 5.565% of the total variance with an eigenvalue of 1.169 and high values of Hg. Factors 3, 4, 5 and 6 might have originated from the same source (anthropogenic) of the heavy minerals in the beach sediments. They can be termed as "intermediate factors" indicating the association of sand with Cd, Sn, Sb and Hg. It seemed that they originated from industrial wastes, but that each came from a different type of waste. Results of PCA analyses were comparable to the dendogram and formed six different clusters in accordance with the factor analysis. Figure 4 shows the dendogram of these six factors.

Based on the average weighs of chemical analyses, chemical parameters and elements with identical status, hierarchical cluster analyses were made for stations and accordingly, the stations sampled were divided into three different groups (Fig. 5). Identical groups were considered to have similar features during contaminations. Stations sampled on the basis of hierarchical cluster analyses for heavy metals were divided into six different groups.

The PCA analyses suggested six groups. The first group included Mn, Ti, Fe, Al, Zn, Cr, V and Cu; the second group included Ni, W, Mg, As and Cl; the third group included Mo, Co and Cd; the fourth group included Sn, Sb and Pb; the fifth group included Hg and the sixth group included Ag only by total Variance Explained and Component Matrix (six factors selected) (Fig. 6).

Fig. 3 Frequency histograms for heavy metals in the study area

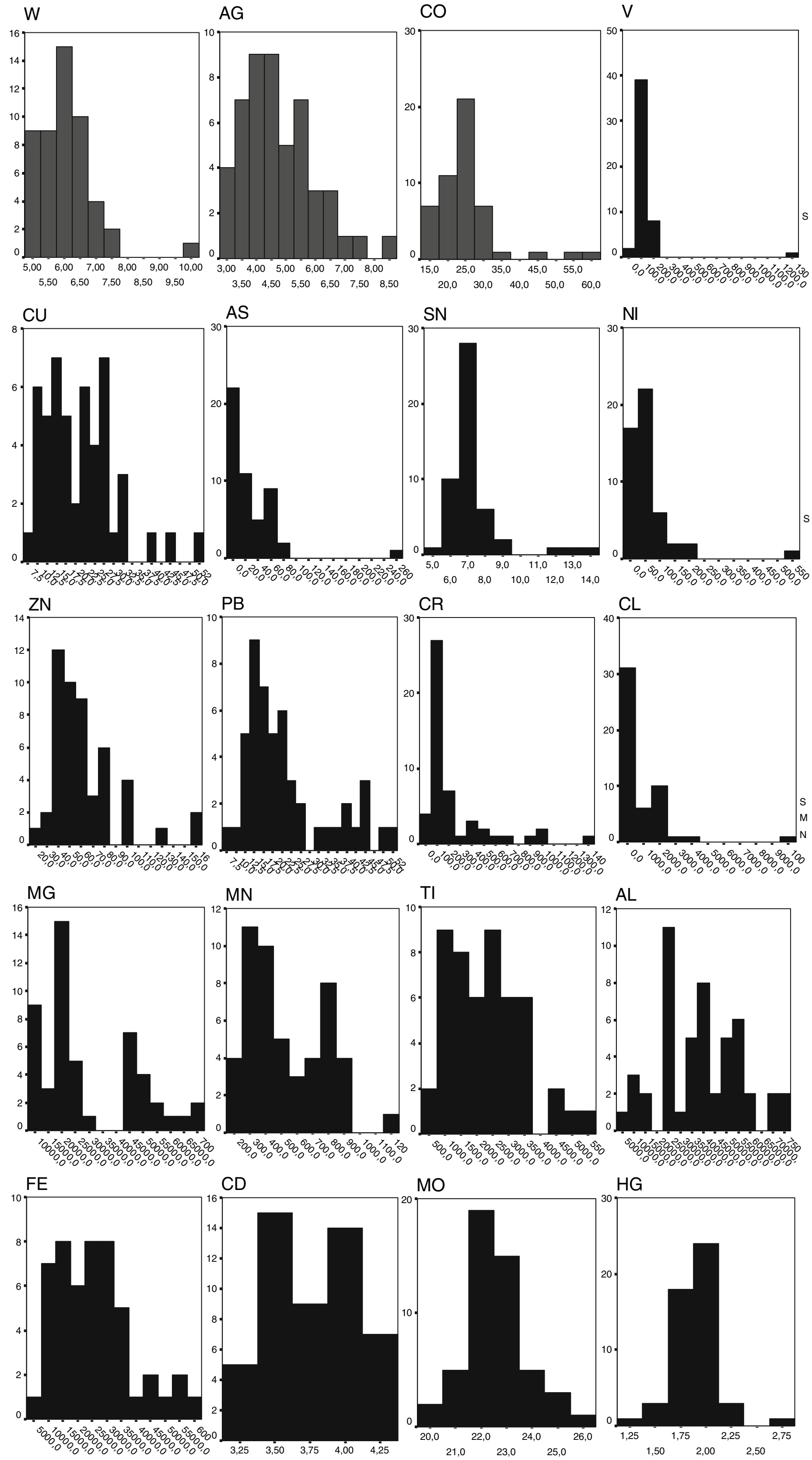

Table 3 Comparison between element concentrations in Kizkalesi Coast, acceptable limit for Turkey, Earth crust and Portugal dune sediment samples (in mg/kg)

	Earth crust (mg/kg) (Krauskopf 1979) (A)	Acceptable limit for Turkey (mg/kg) (B)	Portugal dune sediments (Vidinha et al. 2006) (C)	Kizkalesi coast dune sediments mean (D)	Variation of average concentration in acceptable limit for Turkey (fold) (D/B)	Variation of average cnt. (fold) (D/C)	Variation of average concentration in Earth crust (fold) (D/A)
Zn	70	150	112.8	19.75	−0.13	−0.18	−0.28
Ni	75	30	39.9	186.8	**6.22**	**4.68**	**2.49**
Cu	50	50	361.2	10.13	−0.20	**0.03**	**0.20**
Co	22	20	47	28.2	**1.41**	−0.60	**1.41**
V	110	–	–	63.3	–	–	−0.57
Mo	1.5	10	–	25.96	**2.59**	–	**17.30**
Ag	0.07	–	–	4.13	–	–	**59**
Sb	0.2	–	–	5.95	–	–	**29.75**
Sn	2.5	20	–	8.17	-0.4	–	**3.27**
Cd	0.15	–	–	4.21	–	–	**28**
W	1.2	–	–	7.61	–	–	**6.34**
Hg	0.02	1	–	2.05	**2.05**	–	**102.5**
Pb	12.5	50	71.7	4.55	0.09	−0.06	−0.36
As	1.8	20	–	24.74	**1.13**	–	**13.74**
Al	8.1×10^4	–	61000	8267.17	–	−0.14	−0.102
Fe	5.4×10^4	–	21000	18803.63	–	−0.90	−0.35
Mg	2.3×10^4	–	7000	34993.03	–	**5.00**	**1.52**
Cl	130	25	–	6635.07	**265.4**	–	**51**
Ti	5000	–	–	813.48	–	–	−0.16
Mn	1000	–	369.8	585.99	–	**1.58**	−0.59
Cr	100	100	62.8	553.84	**5.54**	**8.82**	**5.54**

cnt.: concentration

Bold characters are anomaly value

In the Regression analyses of the chemical data on Pb in Kizkalesi coast, calculations were done according to a Model Summary and ANOVA (Table 6). The degree of accuracy of the chemical analyses was found to be at the highest level. The explanatory power of the regression analyses for Model Summary was $R^2 = 100\%$. According to ANOVA, 20 descriptive variables (Cr, Mo, As, Sb, Hg, Cd, Cl, Ag, Cu, Sn, Ti, Mn, Co, W, V, Ni,Zn, Fe and Mg) had a high explanatory power for the variation of Pb element. These results suggested that the number of samples and heavy metals in the study area was sufficient.

The variations in heavy metal contents showed some differences (Fig. 2). In the study area, Al, Fe, Mg and Cl had the highest concentrations, Ti, Mn, Cr and Ni had high concentrations, V, Co, Mo, Zn, As and Cu had low concentrations and Sn, Ag, W, Hg, Pb, Sb and Cd had the lowest concentrations. In this respect, a special attention should be given to highly concentrated heavy metals such as Al, Fe, Mg, Cl, Ti, Mn, Cr and Ni. However, other metals with low concentrations should not be ignored. When compared to earth crust values (Krauskopf 1979), Hg had the highest concentration followed by Ag, Cl, Sb, Cd, Mo, As, W, Cr, Sn, Ni, Mg, Co and Cu and when compared to acceptable concentrations for Turkey, CI had the highest concentration followed by Ni, Cr, Mo, Hg, Co and As in Kizkalesi coast sand. Changes in the heavy metal concentrations in the study area were higher than normal. It is of utmost importance for the environment that invasion of those metals into the area should be stopped. All heavy metals exceeding their cut-off values may be harmful for human health and the environment. Correlation analyses revealed moderate to strong positive relations between the heavy metals. In fact, there were strong positive correlations between **Al** and Fe, Ti, Mn and Cr; between **Fe** and Mg, Ti, Mn and Cr; between **Ti** and Mn and Cr; between **Ni** and W, As and Mg; between **Mn** and Cr and moderate positive correlations between **Mg** and Cl and Cr. The possible sources of heavy metals with positive correlations were considered the same, which was confirmed by the presence of a relation between concentrations of heavy metals. The heavy metals affecting the study area were not supplied from far distances but from close proximity and moderate distances. Particularly Al, Fe, Ti and Mn which showed the highest concentrations were thought to come

Table 4 Coefficient correlation between the elements on dune sediments in the Kizkalesi Coast

	Zn	Ni	Cu	Co	V	Mo	Ag	Sb	Sn	Cd	W	Hg	Pb	As	Al	Fe	Mg	Cl	Ti	Mn	Cr
Zn	1																				
Ni	0.371	1																			
Cu	0.508*	0.491*	1																		
Co	0.222	0.261	0.551*	1																	
V	0.892**	0.232	0.446*	0.175	1																
Mo	−0.052	0.032	0.321	0.686**	−0.063	1															
Ag	−0.179	−0.416	−0.456*	−0.462*	−0.030	−0.171	1														
Sb	−0.084	−0.057	−0.287	−0.079	−0.187	0.091	0.066	1													
Sn	−0.131	0.189	−0.020	0.179	−0.332	0.254	−0.181	0.451*	1												
Cd	0.167	0.273	0.247	0.430	0.061	0.069	−0.548*	−0.155	0.426	1											
W	0.361	0.954**	0.563**	0.425	0.217	0.234	−0.457*	−0.002	0.231	0.337	1										
Hg	0.077	−0.005	0.198	0.173	0.025	0.095	−0.184	−0.034	−0.009	0.002	−0.016	1									
Pb	−0.111	0.145	0.161	0.160	−0.010	0.270	−0.070	0.240	0.241	0.071	0.313	−0.276	1								
As	0.089	0.836**	0.262	0.296	−0.145	0.088	−0.526*	0.031	0.412	0.358	0.785**	0.076	0.003	1							
Al	0.956**	0.416	0.602**	0.335	0.786**	0.012	−0.291	−0.024	−0.027	0.259	0.441	0.097	−0.083	0.143	1						
Fe	0.962**	0.481*	0.535*	0.216	0.868**	−0.123	−0.250	−0.133	−0.145	0.164	0.456*	0.029	−0.100	0.182	0.946**	1					
Mg	0.510*	0.936**	0.481*	0.234	0.382	−0.044	−0.404	−0.091	0.077	0.163	0.881**	0.068	0.042	0.785**	0.519*	0.636**	1				
Cl	0.149	0.403	0.055	−0.215	0.158	−0.086	−0.056	−0.088	0.171	−0.114	0.252	0.050	−0.070	0.449*	−0.019	0.178	0.477*	1			
Ti	0.960**	0.183	0.517*	0.225	0.880**	−0.015	−0.121	−0.091	−0.205	0.097	0.201	0.084	−0.121	−0.131	0.949**	0.922**	0.327	−0.033	1		
Mn	0.942**	0.146	0.483*	0.235	0.868**	0.059	−0.097	−0.032	−0.115	0.139	0.193	0.061	−0.051	−0.156	0.931**	0.887**	0.280	−0.072	0.981**	1	
Cr	0.861**	0.390	0.508*	0.321	0.839**	0.013	−0.138	0.084	−0.124	0.111	0.419	0.198	−0.008	0.068	0.859**	0.870**	0.552*	0.069	0.849**	0.821**	1

* Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed). N: 20

Table 5 Explanation of total variance of sand samples with eigen values (a) and Component Matrix (six factors selected) (b)

Initial eigenvalues (a)

Extraction method, principal component analysis

	Total	% of Variance	Cumulative %
1	7.925	37.740	37.740
2	3.940	18.762	56.502
3	2.211	10.529	67.030
4	1.593	7.583	74.614
5	1.266	6.027	80.641
6	1.169	5.565	86.206

Component matrix (rotated) (b)

	F1	F2	F3	F4	F5	F6
Fe	**0.933**	0.300	−0.055	0.093	−0.098	0.005
Al	**0.941**	0.166	0.086	0.210	0.025	0.041
Zn	**0.964**	0.179	−0.017	0.067	−0.036	0.050
Cr	**0.899**	0.204	0.137	−0.041	0.072	0.078
Ti	**0.985**	−0.040	0.045	0.035	−0.072	0.051
Mn	**0.975**	−0.088	0.083	0.056	0.016	0.001
V	**0.912**	0.063	0.011	−0.109	−0.201	−0.052
Mg	0.372	**0.901**	0.034	0.081	−0.054	−0.003
Cu	0.471	0.329	**0.547**	0.199	−0.281	0.017
As	−0.114	**0.879**	0.069	0.350	0.137	0.092
W	0.236	**0.825**	0.316	0.224	0.035	−0.214
Ni	0.222	**0.914**	0.100	0.181	−0.016	−0.119
Sn	−0.181	0.201	0.103	0.386	**0.750**	−0.035
Ag	−0.078	−0.349	−0.262	−0.664	0.050	−0.139
Mo	−0.066	−0.020	**0.886**	−0.015	0.149	−0.001
Co	0.191	0.089	**0.798**	0.395	−0.028	0.056
Cl	−0.010	**0.665**	−0.228	−0.267	0.040	0.173
Sb	−0.006	−0.051	0.015	−0.167	**0.900**	−0.074
Pb	−0.071	0.094	**0.404**	−0.068	0.228	−0.704
Hg	0.056	0.042	0.254	−0.023	0.039	**0.846**
Cd	0.095	0.084	0.063	**0.916**	0.053	−0.066

Extraction method: Principal component analysis; Rotation method: Varimax with Kaiser normalization

a, Rotation converged in 5 iterations

Bold characters are similar sources in factors

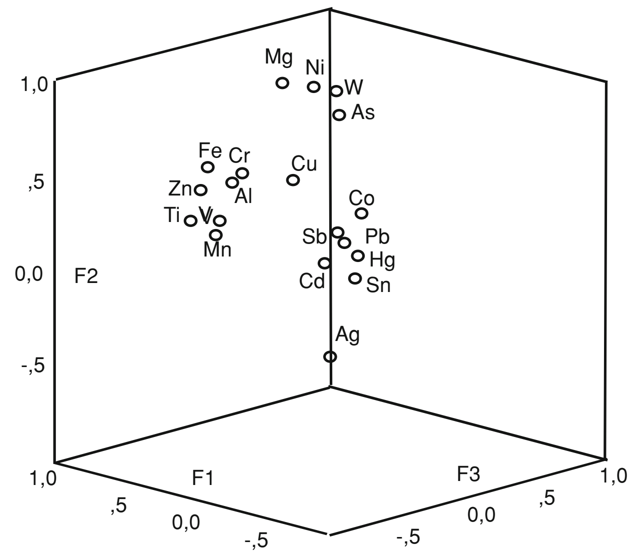

Fig. 4 Principal component analysis loading plot in rotated space (six components extracted)

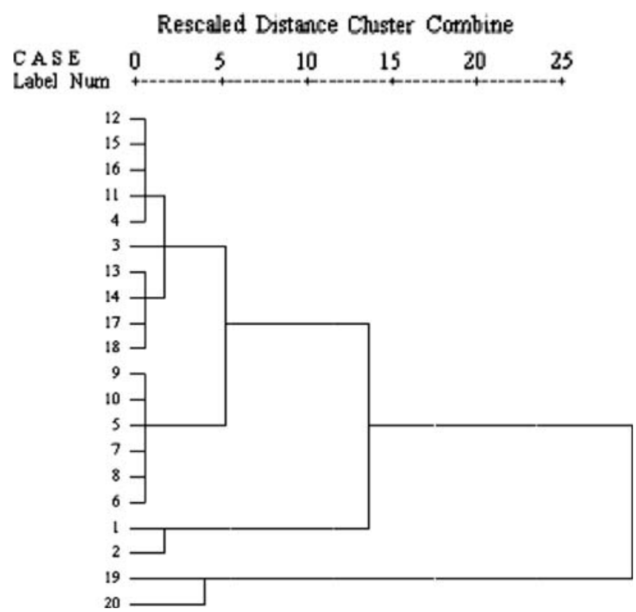

Fig. 5 Hierarchical cluster analysis

from nearby to moderately remote sources and Mg, Cl, Cr and Ni from nearby areas. The basement of the study area was comprised by the Miocene carbonate rocks of the Tauride belt and there was no metal mine in the area. We thought that heavy metal concentrations in the sediments could not have come from present rocks in the area. Therefore, possible sources cannot have a geogenic origin and heavy metal inputs could have an anthropogenic origin.

The heavy metal concentrations of Portugal beach and dune sediments (Vidinha et al. 2006) were higher than those of Kizkalesi area. However, Ni, Mg, Mn and Cr contents of Kizkalesi coast dune sediments were higher. These disparities could be attributed to regional differences.

Principal component analyses of all heavy metals were made (Table 5) and six principal component factors (F1, F2, F3, F4, F5 and F6) were determined. Apart from F1 and F2 factors, the sources of the elements comprising F3, F4, F5 and F6 factors might have been the same. However, F1 factor (Fe, Al, Zn, Cr, Ti, Mn and V; *anthropogenic factor*), F2 factor (Mg, As, W, Ni and Cl; *natural process factor*), F3 factor (Cu, Mo, Co and Pb; *intermediate*

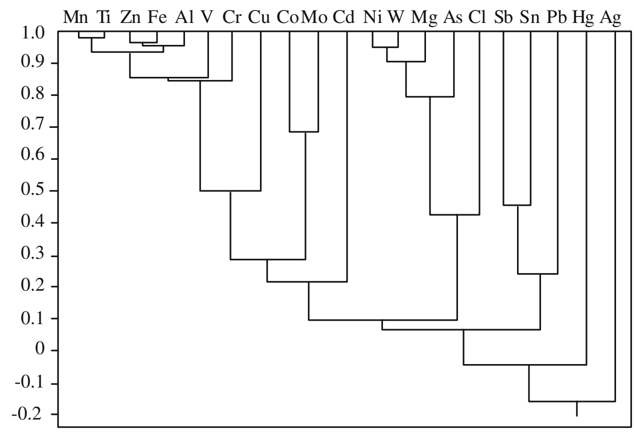

Fig. 6 Element dendogram

factor), F4 factor (Cd; *intermediate factor*), F5 factor (Sn and Sb; *intermediate factor*) and F6 factor (Hg; *intermediate factor*) might have come from a different source and the other metals might have originated from similar sources. Therefore, we used PCA to examine heavy metal contents of dunes. Based on correlation coefficients (Pearson coefficient), Cluster analysis (CA) was conducted with average weighs of chemical analyses, chemical parameters and elements with identical status. This method is the most suitable one to determine the correlation between the variations (Le Maitre 1982). Although it is not notably different from PCA, this method is an alternative to confirm the results (Facchinelli et al. 2001). Therefore, separate Hierarchical Cluster Analyses were performed for elements and stations in the study area. Based on the Hierarchical Cluster Analysis conducted for each sampling station and element, three (3) different groups were formed at a 50% arbitrary similarity of Q-type level (Figs. 5 and 6). Groups of stations revealed similarities in contamination. Groups of elements had the possible sources. The first group of elements included Mn, Ti, Fe, Al, Zn, Cr, V and Cu; the second group included Ni, W, Mg, As and Cl; the third group included Mo, Co and Cd; the fourth group included Sn, Sb and Pb; the fifth group included Hg and the sixth group included Ag. Associations between the elements were found to be consistent with and confirm other statistical data.

The sufficiency of all data from the study area was checked by a Model Summary and ANOVA. The Model Summary was $R^2 = 100\%$. According to ANOVA, 20 descriptive variables had a high explanatory power for the variation of Pb element. These results indicated that the number of samples from the area was sufficient.

Some heavy metals in the beach and dune sediments of Kizkalesi beach showed abnormal values. Concentrations of some metals exceeded the background values. Regression analyses based on Pb values showed that "Model Summary" was significantly sufficient and that "Anova" with 20 explanatory variables was reliable.

Based on the Hierarchical Cluster Analysis dendrogram performed for the stations, contamination was found to occur in three (3) different groups at a 50% arbitrary similarity of Q-type level. According to Pearson's correlation coefficients between the elements, heavy metals in the cluster analysis generally originated from six (6) different sources.

Considering their abundance in the sediments, heavy metal concentrations were ranked from the highest to the lowest as in the following: Al, Fe, Mg, Cl, Ti, Mn, Cr, Ni, V, Co, Mo, Zn, As, Cu, Sn, Ag, W, Hg, Pb, Sb and Cd. According to the earth crust values, Hg had the highest concentration followed by Ag, Cl, Sb, Cd, Mo, As, W, Cr, Sn, Ni, Mg, Co and Cu and according to the acceptable concentrations for Turkey, Cl had the highest concentration followed by Ni, Cr, Mo, Hg, Co and As in Kizkalesi coast. It is required that measures should be taken to stop harmful effects of anthropogenic sources of heavy metals. Otherwise, they may cause serious threats to health and the environment.

At both sides of the coast in the study area, heavy metals had high concentrations. High contents of heavy metals (Zn, Cu, Co, V, Sb, Al, Fe, Ti, Mn and Cr) at KKS1 and KKS2 stations can be attributed to a few sources. In comparison to other stations, these two stations were very close to the Mersin-Antalya road. In addition, this area hosted small cargo boats and at one side of these stations

Table 6 Model summary and anova tables of regression data

Model summary

Model	R	R^2	Adjusted R^2	Std. error of the estimate
1	1.000 (a)	1.000	1.000	0.00414

ANOVA (b)

Model		Sum of squares	df	Mean square	F	Sig.
1	Regression	10.688	18	0.594	34568.045	0.004 (a)
	Residual	0.000	1	0.000		
	Total	10.688	19			

(a) Predictors: (Constant), Cr, Mo, As, Sb, Hg, Cd, Cl, Ag, Cu, Sn, Ti, Mn, Co, W, V, Ni, Zn, Fe, Mg

(b) Dependent Variable: Pb

was an entertainment-resting park while another side was near the Korykos castle, and therefore, heavy metal accumulation was high at KKS1 and KKS2 stations. Significantly high heavy metal concentrations (Ni, Cu, Co, Cd, W, Hg, As, Fe and Mg) were also detected at KKS20, KKS19, KKS18 and KKS 17 stations at the other side of the coast. These stations might have been polluted by intense marine transportation, hotels, entertainment centers and hotel waste disposal sites. Concentrations of Sb, Ag, Mo, Pb and Sn were found to be very high at KKS5, KKS7, KKS8, KKS9 and KKS12 stations respectively. Contamination at these stations was generally due to urban wastes.

Heavy metal accumulation in Kizkalesi coast was of anthropogenic origin and, the contamination originated from accumulating wastes from cargo boats, recent coastal erosion, the Kizkalesi residential site near the shore, uncontrolled urban wastes, Mersin-Antalya road extending parallel to the coast and waste disposal sites of hotels on the coast. In order to prevent heavy metal contamination and to maintain ecologic stability, some immediate measures should be taken and necessary protection sites should be established by conducting new projects around Kizkalesi coastal area.

It can be recommended that accumulation of heavy metals in the region should be stopped. In this context, the highway along the coast should not be used. Instead, another highway should be built. Motor vehicles should not be allowed in the cobblestone pavement near the sea. Large trucks should not be allowed in the residential area of Kızkalesi, either. It is required that precautions should be taken to prevent disposal of household and industrial wastes on the coast and that a waste disposal plant should be built. Tourists' residences and summer houses should be checked more frequently, their wastes should not be disposed into the sea and the waste disposal plant should be built nearby. Waste could be stored somewhere else until the waste disposal plant can be built. Anthropogenic wastes from the residential and nonresidential areas should never be disposed into the streams near and inside Kızkalesi. Ship wastes reaching the coast should also be kept under control. Local authorities should cooperate with coast security units to avoid coastal pollution. An appropriate port for big ships should be built on Kızkalesi coast and small ships should be prevented from anchoring on the coast. Boats for tourists should cruise away from the coast.

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