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Use of Multivariate Statistics Methods to Determine Grain Size, Heavy Metal Distribution and Origins of Heavy Metals in Mersin Bay (Eastern Mediterranean) Coastal Sediments

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The aim of the study was to determine variability, heavy metal content and potential origins of heavy metals of the sediments in a total of 60 locations representing coastal sediments of Mersin Bay. Grain size distribution and heavy metal contents were measured and multivariate statistical analyses were performed on obtained values. In grain size distribution, Oz-4, 5, 6, 11, 12, 13, 14, 15, 16, 18, 19, 22, 23, 46, 48, 49, 50 stations showed a bimodal distribution. This distribution developed due to river networks near the locations. Heavy metals are sequenced as Cr, Mn, Sr, Ni, V, Zn, Co, Zr, Rb, Ce, Cu, Sc, Li, Y, Pb, As, Nb, Mg, Fe, Al, Th and U from the higher value to the lower value according to their abundance. According to frequency histogram, Ni, Fe, Al, which showed the highest concentration values among heavy metals came from short-medium distance; while Cr, Ti and Mn came from short distance. Based on these findings, it should be thought that heavy metal sources affecting study area are in short distances to study area. All the elements were represented with three sector principal component analysis. Total variances of Pb, As, U, Th, Sb, P, La, Ba, Na, K, W, Ce, Li and Rb elements which represent (F1) factor were explained by 30.591 %. Variance of Mn, Fe, V, Ti, Al, Zr, Y, Sc and Hf elements which represent (F2) factor were explained by 18.749 %. Total variance of Mo, U, Sr, Ca, P, Ti, Nb and Ta elements which represent the third factor (F3) were explained by 14.512 %. These data are significantly consistent with the dendongram prepared according to coefitic correlation coefficients. Hierarchical group analysis dendongram showed that Q-type cluster had a 50 % arbitrary similarity level and that contamination generally occurred in group 3. It can be thought that similar groups had the same properties during contamination. In regression data performed according to Fe, "Model summary" (according to $R^2 = 99.8$ value) was significantly adequate for statistical data and "Anova" was highly reliable with 36 explanatory variables. Heavy metals in the study area such as Cr, Mn, Ni, Zn, Co, Cu, Pb, Mg, Al, Cd, Sb and Ti might show toxic effects. Heavy metals such as As, Ag, Fe, Mo and Sn should also be paid attention. Al, Fe, Ti, Mn, Cr, Ni, Co, Pb, Zn and V showed an anomaly according to Kizkalesi and Susanoglu coastal sand. Cr, Ni, Co, Mg, Ti, Fe and Mn increased due to Mersin Ophiolite. The areas where basic/ultrabasic rocks outcropped in the region can be considered as the source of natural contaminations. Anthropogenic factors, coastal sediments, coastal erosion and lithological effects are the main causes of contamination in the study area, which covers a very wide area. In addition, the port, river entrances, highway, urban wastes, tourist facilities and industrial sites increased the density of anthropogenic effect.

Key Words: Heavy metals, Multivariate analysis, Dune sediments, Mersin bay.

INTRODUCTION

Heavy metal contents in coastal sediments due to natural and anthropogenic processes were handled by various scientific studies. These studies provided important information to identify natural and anthropogenic origins of heavy metals[1-10]. There is a large number of literature on biogeochemistry[11], soil parameters[12], stratigraphy[13,14], marine geology and geophysics[15], the effects of sea water[16], costal tourism[17], mediterranean geology[18], heavy metal ratios in northeastern Mediterranean fish[19] and heavy metals in coastal sand of Mediterranean region[20,21] and the vicinity of our study area. However, the literature contains no scientific study on heavy metal contents of coastal sand of Mersin Bay, the origins and distribution of these heavy metals.

The study determined grain size distribution and heavy metal content of Mersin Bay coastal sand and identified geological/anthropogenic origins and mineral contents of heavy metals. Multivariate statistical methods were applied on chemical analysis results to evaluate the origins of heavy metals.

EXPERIMENTAL

Mersin Bay is located between Mersin (Altinkum) and Adana (Karatas) provinces with its approximately 321 km coastal line. The Bay is located in south of Turkey and east of Mediterranean (Fig. 1), on the geographic location of 36-37° N and and 33-35º E. Mersin has a typical Mediterranean climate with hot and dry summers and cool and wet winters. Average rainfall in the last 30 years varied between 450-736 mm. Rainfall observation station data provided by Turkish state meteorological service indicates that mountainous areas had a higher rainfall. Average annual temperature is 18.7 ºC. January and February are the coldest months, while July and August are the hottest months. Prevailing wind direction in coastal sections is southwest-west. Annual wind speed in urban area was measured as 2.1 m/s. Average relative humidity in the last 30 years is 64.1 %. Relative humidity values are quite similar throughout the year, varying between 60.0-66.6 %. In the region number of cloudy days in 40.7; average sea water temperature is measured as 20.8 ºC.

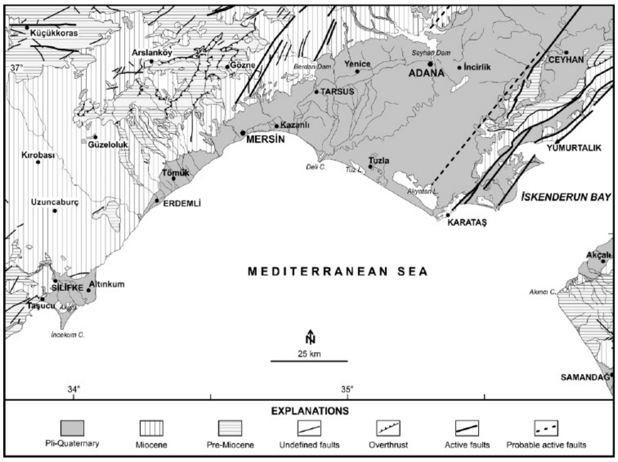

Fig. 1. Areas of the present study and geological map of Mersin Bay (1:500,000)[22,23]

The study region is located in southern part of Miocene carbonate rocks of the Tauride belt. Depositional environments of the sedimentary rocks in the central Tauride belt are described as "unit"[24,25]. 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 old topography and units were not significantly disturbed[26]. The Bolkar Dagi unit is represented by carbonate and clastic rocks together with olistostrome rocks with ages changing from Devonian to lower Tertiary. In addition, the Mersin Ophiolite is also exposed in an area close to the Susanoglu coast. The Bozkir unit is composed tuff, basic, ultrabasic rocks (Mersin ophiolite) and serpantinite and also shelf units and oceanic crust rocks of Triassic-Senonian age[27]. The Mersin ophiolite, represented by approximately 6-km thick oceanic lithospheric section on the southern flank of the Taurus calcareous axis, formed in the Mesozoic Neo-Tethyan ocean some time during late cretaceous in southern Turkey[28] (Fig. 1).

From a total of 60 locations distributed along Mersin Bay which has a length of approximately 321 km, 2-5 kg of coastal sand samples were systematically collected from 10 cm deep pits using plastic gloves. The pits were opened in parallel to the sea at a distance of 5-20 m to the sea. The coordinates were determined with GPS (Garmin Colourado 300) in sample collection areas. The samples whose coordinates were determined with GPD were marked on 1/100.000 scale map. Formation controls were performed for locations and photographs were taken. After laboratory studies, anomaly maps were drawn using Arcwiew-Freehand Software. Analysis results were interpreted on graphs. Laboratory studies included the studies performed on the samples collected from the study area. Grain size distribution and loss on ignition of coastal sand samples were measured. The samples were first spread on a clean paper under laboratory conditions and were left to drying at room temperature for 3 days. Dried coastal sand samples were then measured in analytical balance and 100 g of sample were put into two bags. One bag was measured for grain size distribution; other bag was measured for preparation for chemical analysis.

Grain size of the samples spared for grain size distribution was identified by passing the samples from jigging screens. A total of 60 samples were passed from jigging screens and the weight of grain size passing each screen was measured. The names of columns, sieve sizes (mm) and grain names in grain size distribution are listed as; first column pebble (> 4), second column granule (4.0-2.0), third column vcs (2.0-1.0), fourth column *cs* (1.0-0.5), fifth column ms (0.5-0.25), sixth column fs (0.25-0.125), seventh column vfs (0.125-0.0625), eighth column silt + clay (0.0625<). Fine and glossy sections of the samples were enriched by precipitation with bioform were performed in the laboratory of our university. Mineral identifications of fine sections and glossy sections were performed using Nikon Pol-400 microscope in our laboratory. Of the coastal sand samples, 5 (five) were screened with 0.0625-0.5 mm screens and were collected for petrographic studies. The procedure was defined by Lewis *et al.*[29] and Grosz *et al.*[30]. Standard petrographic techniques were applied on the samples whose fine and glossy sections were prepared. The grains were identified with point counter (a total of 300 mineral-rock grains) and number percentages were converted into figure percentages.

Coastal sand samples prepared for chemical analysis was dried in incubator at 5 ºC for 24 h and loss on ignition was measured. The measurements were performed with analytical balance. The samples were homogenized in agate mortar and were sent to "Canada-Acme Lab. Co." for chemical analyses. In this laboratory, the samples were analyzed with ICP-MS 1EX method and heavy metal contents were measured. MS Excel and SPSS (software 11.5) software were applied on chemical analysis results respectively. These applications were performed by using simple statistical and multivariate analysis techniques.

RESULTS AND DISCUSSION

Losses on ignition values were calculated to identify water and humidity ratio in grain surface of sand samples. It was found that loss on drying of sample no Oz-57 and all samples between sample no Oz-1 to sample no Oz-50 was 0-5 %; loss on drying of sample no Oz-55 and Oz-60 was 5-10 % and loss on drying of sample no Oz-51, 52, 53, 54, 56, 58, 59 were higher than 10 %.

Oz-1, 2, 3, 7, 20, 21, 28, 30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 47, 51, 52, 55, 56, 57, 58 and 59

TABLE-1
STATISTICAL SUMMARY IN THE MERSIN BAY BEACH AND ABUNDANCE OF HEAVY ELEMENTS

	Mean (A)	Earth crust (mg/kg) [33] (B)	Variation of average concentration in Earth crust (fold) (A/B)	Sanstone [34] (C)	Variation of average concentration in Sanstone (fold) (A/C)	Ultrabasic [34] (D)	Variation of average concentration in Ultrabasic (fold) (A/D)	Acceptable limit for Turkey (mg/kg) [35] (E)	Variation of average concentration in TKKY (fold) (A/E)	Kizkalsi Beach sediman Mean [20] (F)	Variation of average concentration in Kizkalesi Beach dune (A/F)	Susanoglu Beach sediman Mean [21] (G)	Variation of average concentration in Susanoglu Beach dune (A/G)	Iskenderun Beach sediman Mean (Yalcin. 2008)(G)	Variation of average concentration in Iskenderun Beach dune (A/G)
Al	30485	81000	0.376	25000	1.219	20000	1.524			8267	3.687	11924	2.556	26648	1.143
Fe	34078	54000	0.631	9800	3.477	94300	0.361			18803	1.812	13909	2.450	45312	0.752
Mg	42370	23000	1.842	7000	6.052	204000	0.207			34993	1.210	15624	2.711	93500	0.453
Ti	2772	5	554. 400	1500	1.848	300	9.240			813	3.409	736	3.766	2414	1.148
Mn	7666000	1000	7666	90	85177.77	1620	4732.098			585	13104.273	333	23021.021	1166	6574.614
Cr	15124100	100	151241	35	432117.142	1600	9452.562	100	151241	553	27349.186	428	35336.682	1187	12741.449
Cu	158517	50	3170. 340	9	17613.0	10	15851.7	50-140	3170.340-1132.264	10	15851.7	12	13209.750	16	9907.312
Ni	2790920	75	37212. 266	2	1395460.0	2000	1395.460	30-75	93030.66-37212.266	186	15004.946	145	19247.724	646	4320.309
Co	281217	20	14060. 850	0.3	937390.0	150	1873.780	20	14060.850	28	10043.464	21	13391.285	43	6539.930
Pb	102300	12.5	8184.0	7	14614.285	1	102300	50-300	2046.0-341.0	4	25575.0	5	20460.0	15	6820.0
Zn	525500	70	7507. 142	16	32843.750	50	10510.0	150-300	3503.3-1751.666	19	27657.894	17	30911.764	89	5904.494
Cd	2127	0.15	14140.0	0.09	23633.333	0.9	2363.3	1-3	2127-709.0	4	531.750	4	531.750	0.3	7090.0
As	88833	1.8	49351.666	1	88833	1	88833	20	4441.650	24	3701.375	19	4675.421	9.7	9158.041
Ag		0.07		0.09		0.06				4		4		0.1	
Mo	4980	1.5	3320.0	0.2	24900.0	0.3	16600.0	10	498	25	199.200	27	184.444	0.7	7114.285
Sb	3433	0.2	17165.0	0.09	38144.444	0.1	343.3			5	686.600	5	686.600	0.4	8582.500
Sn	8350	2.5	3340.0	0.9	9277.777	0.5	16700.0	20	417.500	8	1043.750	7	1192.857	1.2	6958.33
V	1141170	110	10374.272	20	57058.500	40	28529.250			63	18113.809	38	30030.789	122	9353.852
W	3116	1.2	2596.666	1.6	1947.500	0.77	4046.753			7	445.142	6	519.333	1.4	2225.714

concentrated in column six (0.25 mm-0.125 mm). Oz-9, 25, 27 and 29 concentrated in column five (0.5 mm-0.25 mm). Coastal sand in the study area generally presented a one type aggregation and a highly good sorting was observed. Oz 8, 10, 15, 19, 24, 27, 30, 53 and 54 concentrated on column four (1.0 mm-0.5 mm), column five (0.5 mm-0.25 mm) and column six (0.25 mm-0.125 mm) and showed a negative thin skewness. Oz-4, 5, 6, 11, 12, 13, 14, 15, 16, 18, 19, 22, 23, 46, 48, 49 and 50 showed a bimodal distribution. There might be an entrance of a small river into the coastal sand in the region. Oz-17, 22 showed as a bad sorting by distributing to all columns. Oz-26 showed a positive and thick skewness. Oz-31 showed a negative skewness and a bad sorting. Oz-60 concentrated in column one (›4 mm), column two (4.0 mm-2.0 mm), column three (2.0 mm-1.0 mm), column four (1.0 mm-0.5 mm) and showed positive thick skewness.

Various scientific studies on geology used statistical applications[31]. Particularly geochemical studies have a wide application area. Multivariate statistical methods proved to be highly successful particularly in identification of the origins of heavy metal contents in soil[32]. In this context, the present study conducted statistical studies based on the geological data in the study area. Heavy metal contents of sand samples collected from Mersin Bay were presented in Table-1. Simple statistical evaluations were performed on chemical analysis results. According to arithmetical averages, heavy metals can be listed from the highest to the lowest as Cr, Mn, Sr, Ni, V, Zn, Co, Zr, Rb, Ce, Cu, Sc, Li, Y, Pb, As, Nb, Mg, Fe, Al, Th and U. Arithmetic averages of heavy metals were 1512.41, 766.6, 329.4, 279.092, 114.117, 52.55, 28.1217, 25.1117, 23.8367, 21, 15.8517, 13.1, 10.5483, 10.4417, 10.23, 8.88333, 5.445, 4.237, 3.40783, 3.0485, 2.52333, 1.005 and minimum-maximum presence ratio were 34-9472, 213-1333, 162-886, 41.1-860.3, 23-359, 19-211, 4.8-70.3, 11.2-54.3, 4.7-56.6, 6-55, 4.7-250.7, 2-36, 4.9-15.9, 5.7-16.4, 2.2-100.5, 2-24, 1.9-30.6, 1.35-10.48, 0.86-7.06, 1.21-4.3, 0.4-5.8, 0.5-1.8 respectively (Fig. 2).

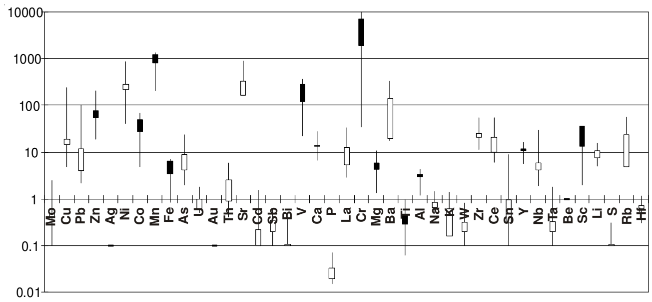

Fig. 2. Heavy metal concentrations in beach and dune sediments

Order of significance of heavy metals according to their abundance was determined based on this sequence. In many locations in the study area, certain heavy metals showed high levels.

The stations which gave high anomaly in terms of heavy metal content were found to be; Oz 1 (Merdivenli Kuyu Mahallesi Beach), Oz 2 (Yemiskumu mahallesi Beach), Oz 3 (Kumkuyu Beach), Oz 11 (Arpacbahsis Beach), Oz 12 (Tumuk Beach), Oz 13 (Uzmez Tatil Sitesi Beach: onemli), Oz 14 (Flamingo 9 sitesi Beach), Oz 26 (Mersin Limani uç noktasi Beach), Oz 30 (Karaduvar mahallesi Beach: onemli), Oz 33(Kozanli lisesinin onu), Oz 47 (Tuzla Beach), Oz 55 (Akyatan golu alti Beach), Oz 29 (Karaduvar Beach), Oz 35 (Domuz Golu Beach), OZ 36 (Acigol Beach) stations in the study area (Table-1).

According to chemical analysis results, arithmetic averages of some heavy metals in coastal sand of Mersin Bay exceeded Mg, Ti, Mn, Cr, Ni, Co, Pb, Zn, As, Sb, V, W values according to earth's crust (mg/kg); Al, Fe, Mg, Na, Ti, Mn, Cr, Ni, Co, Pb, Zn, Cd, As, Ag, Mo, Sb, Sn, V and W values according to sandstones[33]; Al, Ca, Na, K, Ti, Cu, Pb, Cd, Zn, As, Ag, Mo, Sb, Sn, V and W values according to ultrabasics[34]; Cr, Ni and Co values according to acceptable limit values for Turkey[35]; Al, Fe, Ti, Mn, Cr, Ni, Co, Pb, Zn and V values according to Kizkalesi coastal sand[20]; Al, Fe, Mg, Ti, Mn, Cr, Cu, Ni, Co, Pb, Zn and V values according to Susanoglu coastal sand[21].

According to these analysis results, heavy metal concentration values (Zn, Ni, Cu, Co, V, Mo, Ag, Sb, Sn, Cd, Cd, W, Hg, Pb, As, Al, Fe, Mg, Cl, Ti, Mn, Cr) elements, were found to be higher when compared to Kizkalesi and Susanoglu coastal sand, earth's crust, sandstone, acceptable limit values for Turkey. In short, Cr, Mn, Ni, Zn, Co, Cu, Pb, Mg, Al, Cd, Sb and Ti heavy metals which showed higher values when compared to similar studies show a similarity with the metals which are abundant in the region. For this reason, these heavy metals might have potential toxic effects in the region. In addition, heavy metals such as As, Ag, Fe, Mo and Sn which showed anomaly when compared to other studies are also present. The effects of all of these heavy metals to environment and human health should be paid more attention.

Frequency histogram of each element was analyzed. According to frequency histogram, it was thought that Mo, Cu, Pb, Zn, Ag, Mn, Th, Cd, Sb, Bi, V, Cr, Ti, W, Ce, Sn, Nb and Ta contents came from areas of short distance; Ni, Fe, As, U, Sr, Al, K, Zr, Y, Sc, Li, Rb and Hf contents came from medium-short distances and Mg came from a medium distance. Accordingly, it should be thought that the sources of heavy metals affecting the study area are located in short distances. In addition, it can be stated that heavy metals come from short and medium distances. It was found that particularly Ni, Fe, Al which showed the highest concentration values among heavy metals came from short-medium distance; while Cr, Ti and Mn came from short distance (Fig. 3).

With reference to the correlation matrix which indicates the correlation among different elements. Correlations were analyzed for the heavy metals with potential toxic effects (Cr, Mn, Ni, Zn, Co, Cu, Pb, Al, Cd, Sb, Ti, As, Fe, Sn). The positive high relationship (r^2 = less than 0.01) among sand *vs.* contaminated elements. (Cr *vs.* Mg, Ti, Sc; Mn *vs.* Fe, V, Cr,

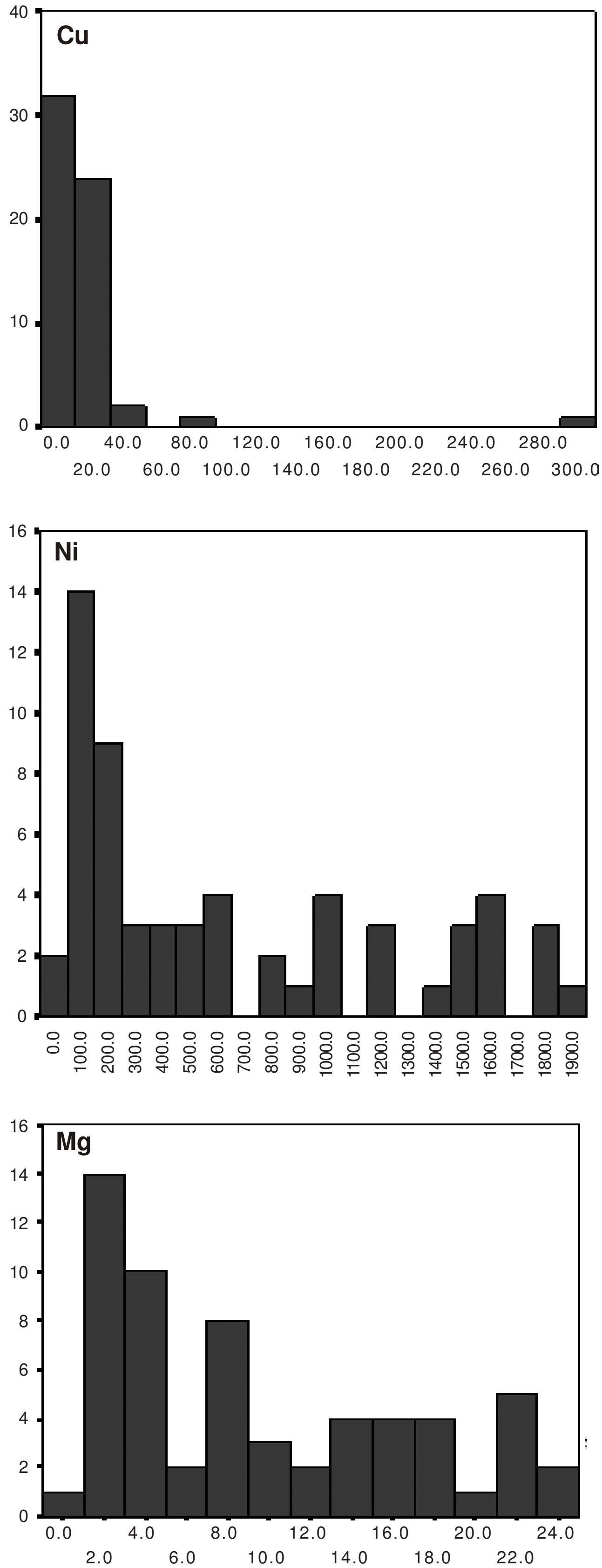

Fig. 3. Frequency histograms for heavy metals in the study area

Mg, Ti, Y, Ta, Sc, Nb, Hf; Ni *vs.* Co, Mg; Zn *vs.* Co, Fe, Cd, V, Cr, Ti, Sn, Nb, Ta; Co *vs.* Mn, Fe, V, Cr, Mg, Ti, Y, Nb, Sc; Cu *vs.* Pb, Zn, Sn; Pb *vs.* Zn, Cd, Sb, Sn; Al *vs.* W, Zr, Ce, Y, Li, Rb, Hf; Sb *vs.* La, Ba, Al, W,Ce, Li, Rb; Ti *vs.* Y, Nb, Ta, Sc, Hf; As *vs.* Th, Sb, Ba, Al, W, La, Rb; Fe *vs.* V, Cr, Mg, Ti, Y, Nb, Ta, Sc; Sn *vs.* Hf) indicates the presence of these elements in sand layers. The association of these elements (Cr, Ni, Co, Mg, Ti, Fe, Mn) are absorbed from ophiolitic materials in the beach sediments rather than finer particles. The above correlation of elements clearly indicates that they are geological in nature. Since there was a consistence between Cr, Ni, Co, Mg, Ti, Fe and Mn ratios and Mersin Ophiolite ratios, it was understood that natural source that affected bay coastal sediments were basic/ultra basic rocks.

Principal component analysis provided important data to identify toxic elements in the soil[36,37]. Principal component analysis results for chemical analysis results of the study area were presented in Table-2. All elements were represented by three factor with their similar properties. It is understood from the table that total variance was explained by 63.852 %. All of the elements were represented by three principal components. Total variance and component matrix analysis (PC) results for chemical analysis results are presented in Table-3. All of the elements were represented by three total variance and component matrix. It is thought that the elements that represented the factor had the same origins.

TABLE-2
TOTAL VARIANCE OF SEDIMENTS WITH EIGEN VALUES (PCA)

	Initial eigenvalues (extraction method: principal component analysis)		
Component	Total	Variance (%)	Cumulative (%)
1	11.013	30.591	30.591
2	6.750	18.749	49.340
3	5.224	14.512	63.852

Based on initial component matrix indicators, the first factor (Factor 1) explains 30.591% of the total variance with a high Eigen value of 11.013 (Table-3). The first factor can be termed as natural process factor. This is clearly identified by the association of Pb, As, U, Th, Sb, P, La, Ba, Na, K, W, Ce, Li, Rb. Furthermore, F1 contains certain amount of Hf and Sr contained by other factors. The second factor (Factor 2) explains 18.749 % of the total variance with a Eigen value of 6.750 (Table-3). This is clearly identified by the association of Mn, Fe, V, Ti, Al, Zr, Y, Sc and Hf. This factor can be termed as anthropogenic factor. The third factor (Factor 3) explains 14.512 % of total variance with an Eigen value of 5.224 (Table-3). This factor can be termed as intermediate factor indicating the association of Mo, U, Sr, Ca, P, Ti, Nb and Ta.

Based on average weights of chemical analysis results, related elements and chemical parameters, it can be thought that three different factors were formed and similar factors showed similar properties during contamination. The first factor (F1 factor) includes K, Rb, Ba, Th, La, Ce, Sb, W, Al, Na, Li and As; the second factor (F2 factor) includes Mn, Fe, V, Ti, Sc, Co, Cr, Y, Zr, Hf, Ni and Mg; the third factor (F3 factor) includes Cu, Pb, Sn, Zn, Cd, Ca, Nb, Ta, U, Sr, P and Mo (Fig. 4). According to chemical analysis results performed for the stations, there was a significant similarity between Mn and Fe; Co and Cr; Ni and Mg; Ni and Mg in the second factor and Cu and Pb; Nb and Ta; U and Sr in the third factor. There was a significant similarity between the combinations that formed in element dendogram and principal component analysis and component matrix analysis groups. This is an important finding for the interpretation of origins. It was believed that origins of the elements in similar groups were the same.

TABLE-3
RESULTS OF FACTOR ANALYSIS FOR BEACH SEDIMENTS IN THE MERSIN BAY

	Component Matrix (a)			Rotated Component Matrix (a)		
	1	2	3	1	2	3
Mo	.185	-.029	.501	-.404	.430	-.407
Cu	-.671	.142	-.208	.370	-.337	.326
Pb	.571	-.083	.155	-.121	.401	.229
Zn	-.227	.285	.310	-.557	-.183	-.129
Ni	-.395	-.452	.010	-.436	.674	-.257
Co	-.772	.337	-.022	-.062	.959	-.077
Mn	-.559	.781	.083	-.078	.962	-.099
Fe	-.581	.774	.067	.288	-.424	.107
As	.479	-.206	-.042	.321	-.301	.802
U	.665	-.063	.625	.900	-.189	.129
Th	.858	.315	-.162	-.069	-.160	.879
Sr	.305	-.146	.830	-.020	-.128	.252
Cd	.129	-.112	.226	.753	-.147	.233
Sb	.752	.277	-.016	.060	.939	-.146
V	-.474	.825	-.020	-.422	-.033	.569
Ca	-.141	-.233	.655	.331	-.057	.737
P	.528	.147	.595	.805	.011	.407
La	.769	.444	.157	-.255	.691	-.125
Cr	-.594	.450	.054	-.548	.199	-.282
Mg	-.630	-.126	-.083	.849	-.394	.029
Ba	.889	.112	-.272	.238	.841	.406
Ti	-.106	.852	.437	.770	.358	-.396
Al	.310	.698	-.544	.653	-.071	-.393
Na	.434	.271	-.569	.865	-.417	-.039
K	.892	.098	-.344	.751	-.067	.034
W	.647	.338	-.192	.562	.258	-.059
Zr	.301	.512	-.179	.822	.057	.376
Ce	.750	.491	.129	.094	.009	.452
Sn	.215	.071	.403	.227	.749	.106
Y	-.163	.759	.143	.104	.238	.858
Nb	.236	.282	.817	.135	.189	.856
Ta	.285	.257	.799	.074	.892	-.285
Sc	-.483	.789	-.162	.577	-.500	-.074
Li	.692	-.124	-.307	.869	-.425	-.030
Rb	.902	.094	-.338	.620	.344	.035
Hf	.334	.619	-.094	-.010	-.046	.532
Extraction method: Principal component analysis. A3 components extracted				Extraction method: Principal component analysis. Rotation Method: Varimax with Kaiser Normalization. a Rotation converged in 5 iterations		

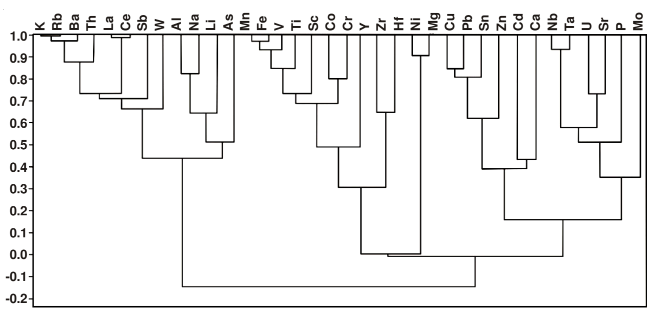

Fig. 4. Element dendograms

Hierarchical group analysis was performed for sample stations considering average weights of chemical analysis results, related elements and chemical parameters (Fig. 5). According to hierarchical group analysis dendogram, Q-type cluster showed a 50 % arbitrary similarity and contamination generally occurred in three clusters. It can be suggested that similar groups show similar properties during their combination. Hierarchical group analysis was performed for sample stations using average weights of chemical analysis results, related elements and chemical parameters. Exclusion of excessive groups in hierarchical group analysis showed that the stations had similar properties, which will further strengthen the accuracy of results since we cannot evaluate different environmental conditions in the evaluations. In the study area, there is a significant similarity between Oz 2, 11, 12, 17, 18, 19 and 47 stations. According to hierarchical group analysis, there were 3 groups of arbitrary similarity and contamination between the locations (Fig. 5).

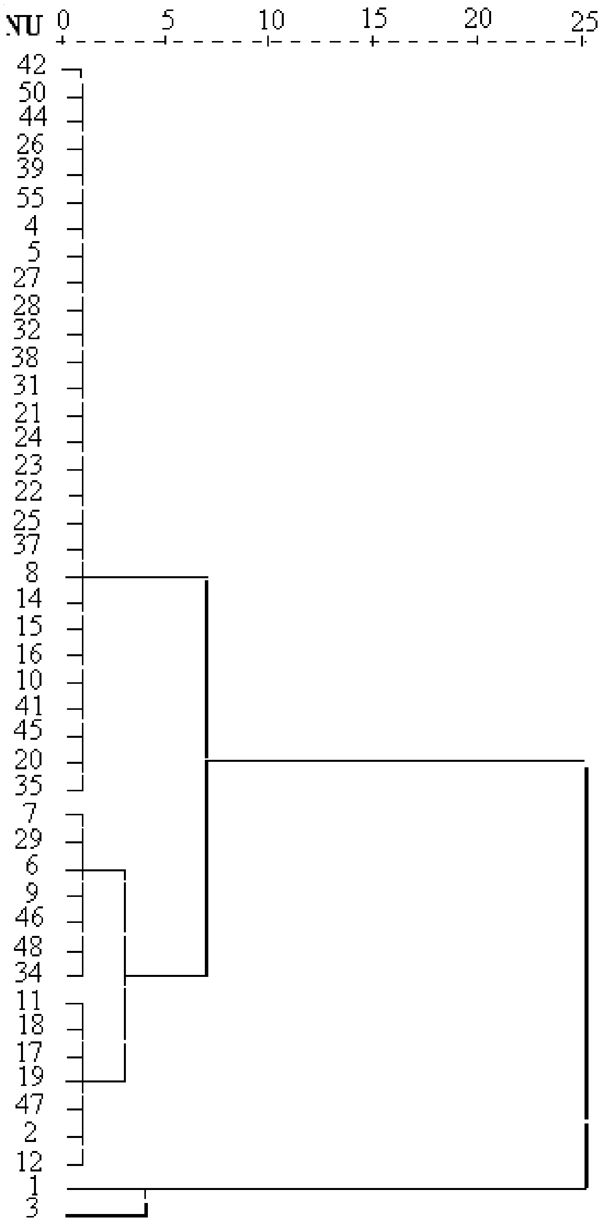

Fig. 5 Hierarchical Cluster analyzes dendogram

In regression data of chemical analysis results performed according to Fe, calculations were made according to model summary and Anova (Table-4). Explanatory percentage of regression equation for model summary was $R^2 = 99.8$ % which provides a significant level of accuracy. According to Anova, 36 exploratory variable significantly explained the variance of Fe elements. Regression data of chemical analysis results showed that model summary was significantly adequate and Anova was highly reliable.

TABLE-4
MODEL SUMMARY AND ANOVA TABLES OF REGRESSION DATA FROM DUNE SEDIMENTS FROM THE MERSIN BAY

Model Summary						
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate		
1	.999(a)	.998	.988	.13892		
ANOVA (b)						
Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	67.733	35	1.935	100.282	.000(a)
	Residual	.154	8	.019		
	Total	67.887	43			

[a]Predictors: (Constant), Hf, Sr, Zn, Sb, N?, Mn, Sn, As, Mo, P, Zr, Li, Ca, Cu, W, Cr, Na, Th, U, Cd, Y, Ta, Ti, K, Sc, La, Al, Ba, Pb, Nb, Co, Mg, Ce, V, Rb; [b]Dependent Variable: Fe

Numerical petrology as suggested by LeMaitre[38]was used in petrographic definitions. Mineral grains were identified in petrographic analysis performed on cross-sections of the samples. Petrographic analysis showed that cross-section no Oz-41 contained 4 zircon, 5 opaque mineral, 3 rutile, 7 olivine mineral grains along one line. Oz-41 contained high amounts of zircon mineral with high pleocroism. High amounts of hornblende, ferromagnetic minerals were formed by strong weathering. Rutile, which is red in colour, shows a high level of pleocroism. The cross-section mainly contained opaque minerals. Cross-section no Oz-35 contained 1 zircon, 2 opaque mineral, 2 rutile, 3 tourmaline, 2 olivine minerals. Cross-section no Oz-35 contained zircon with high pleocroism, tourmaline, rutile and opaque minerals. Oz-53 contained olivine whose interference colour included exponential colours of 2. line. Ultramafic rock parts contained olivine. Shell fragments on it (nummulites; upper paleocene-lower oligocene aged, mussel fragments and other forominifera) were caused by limestone particles. Red-coloured rutile showed a high pleocroism and was abundant in the cross-section.

Conclusion

Grain size distribution and heavy metal contents were measured and multivariate statistical analyses were performed on obtained values. In grain size distribution, Oz-4, 5, 6, 11, 12, 13, 14, 15, 16, 18, 19, 22, 23, 46, 48, 49, 50 stations showed a bimodal distribution. This distribution developed due to river networks near the locations. Heavy metals are sequenced as Cr, Mn, Sr, Ni, V, Zn, Co, Zr, Rb, Ce, Cu, Sc, Li, Y, Pb, As, Nb, Mg, Fe, Al, Th and U from the greatest value to the smallest according to their abundance. According to frequency histogram, Ni, Fe, Al which showed the highest concentration values among heavy metals came from short-medium distance; while Cr, Ti and Mn came from short distance. Based on these findings, it should be thought that heavy metal sources affecting study area are in short distances to study area. All of the elements were represented with three sector principal component analysis. Total variances of Pb, As, U, Th, Sb, P, La, Ba, Na, K, W, Ce, Li and Rb elements which represent factor-1 were explained by 30.591 %. Variance of Mn, Fe, V, Ti, Al, Zr, Y, Sc and Hf elements which represent factor-2 were explained by 18.749 %. Total variance of Mo, U, Sr, Ca, P, Ti, Nb and Ta elements which represent the third factor-3 were explained by 14.512 %. These data are significantly consistent with the dendongram prepared according to coefitic correlation coefficients.

Hierarchical group analysis dendongram showed that Q-type cluster had a 50 % arbitrary similarity level and that contamination generally occurred in group 3. It can be thought that similar groups had the same properties during contamination. In regression data performed according to Fe, Model summary (according to $R^2 = 99.8$ value) was significantly adequate for statistical data and Anova was highly reliable with 36 explanatory variables. Heavy metals in the study area such as Cr, Mn, Ni, Zn, Co, Cu, Pb, Mg, Al, Cd, Sb and Ti might show toxic effects. Heavy metals such as As, Ag, Fe, Mo and Sn should also be paid attention. Al, Fe, Ti, Mn, Cr, Ni, Co, Pb, Zn and V showed an anomaly according to Kizkalesi and Susanoglu coastal sand. Cr, Ni, Co, Mg, Ti, Fe and Mn increased due to Mersin Ophiolite. The areas where basic/ultrabasic rocks outcropped in the region can be considered as the source of natural contaminations. Anthropogenic factors, coastal sediments, coastal erosion and lithological effects are the main causes of contamination in the study area, which covers a very wide area. In addition, the port, river entrances, highway, urban wastes, tourist facilities and industrial sites increased the density of anthropogenic effect.

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REFERENCES

1. M.A. Mange-Rajetzky, *Mar. Geol.*, **52**, 1 (1983).
2. J.K. Rigler and M.B. Collins, *Geol. Mar. Lett.*, **3**, 43 (1984).
3. J.D. Grigsby, *J. Sediment Petrol.*, **62**, 331 (1992).
4. N.G. Razjigaeva and C. Hallswort, *J. Sediment Petrol.*, **62**, 802 (1992).
5. A.C. Marton and C. Hallswort, *Sediment Geol.*, **90**, 241 (1994).
6. G. Anfuso, M. Ahab, G. Coltrane and F. Lopez-Ague, *Bol. Inst., Esp. Oceanogr.,* **15**, 243 (1999).
7. C.W. Hoffman, A.E. Grosz and J.G. Nickerson, *Geotechnol*, **17**, 173 (1999).
8. O.E. Frihy and K.M. Dewidar, *Mar. Geol*., **199**, 27 (2003).
9. M.W. Hounslow and A.C. Marton, *Sediment Geol.*, **171**, 13 (2004).
10. N. Okay and B. Ergun, *Marine Geol.*, **216**, 1 (2005).
11. A.B. Yilmaz, *Environ. Res.*, **92**, 277 (2003).
12. M. Okyar, Geophysical Approach. Ph.D. (Turkish) (1991).
13. M. Okyar, M. Ergin and G. Evans, *Marine Geol.*, **220**, 113 (2005).
14. M. Ergin, K. Timur, M. Okyar, M.N. Bodur and V. Ediger, Technical Report, Institute of Marine Sciences, Middle East Technical University, Erdemli, Mersin, p. 43 (1989).
15. Z. Demirel, *J. Environ. Manage.*, **70**, 275 (2004).
16. S. Burak, E. Dogan and C. Gazioglu, *Ocean Coast. Manage.*, **47**, 515 (2004).
17. V. Ediger, A.F. Velegrakis and G. Evans, *Marine Geol.*, **192**, 321 (2002).
18. H.Y. Cogun, T.A. Yuzereroglu, O. Firat, G. Gok and F. Kargin, *Environ. Monit. Asses.*, **121**, 431 (2006).
19. A. Everest and L. Seyhan, *Build. Environ.*, **4**, 837 (2006).
20. M.G. Yalcin and S. Ilhan, *Bull. Environ. Contaminat. Toxicol.*, **81**, 57 (2008).
21. M.G. Yalcin, *Environ. Geol.*, **58**, 119 (2009).
22. A.M.C. Sengor, Biannual Petroleum Congress of Turkey, 7, pp. 50-64 (1987).
23. MTA, (General Directorate of Mineral Research and Exploration), 1:500,000 Scale Geological Maps of Turkey, Adana Plate. Ankara, No. 15 (2002)
24. N. Ozgul, *Bull. Geol. Soc. Turkey*, **14**, 85 (1971).
25. N. Ozgul, *Bull. Geol. Soc. Turkey*, **19**, 65 (1976).
26. A. Gedik, S. Birgili, H. Yilmaz and R. Yoldas, *Bull. Geol. Soc. Turkey*, **22**, 7 (1979).
27. N. Ozgul and H. Kozlu, *TAPG Bull.*, **14**, 1 (2002).
28. O. Parlak, M. Delaloye and E. Bingol, *Geol. Rundschau*, **85**, 647 (1996).
29. D.W. Lewis, Practical Sedimentology. Hutchinson Ross, Stroudsburg, Pennsylvania, p. 227 (1984).
30. A.E. Grosz, Jr. C.R. Berquist and C.T. Fisher, *Min. Res. Publ.*, **103**, 13 (1990).
31. J.C. Davis, Statistics and Data Analysis in Geology, Wiley Inc, NY, edn. 2 (1986).
32. A. Facchinelli, E. Sacchi and L. Mallen, *Environ. Pollut.*, **114**, 313, (2001).
33. K. Krauskopf, Introduction to Geochemistry, McGraw-Hill Book Company, New York, 123 (1979).
34. K.K. Turekian and K.H. Wedepohl, *Geol. Soc. Am. Bull.*, **72**, 175 (1961).
35. TKKY, Toprak Kirliliginin Kontrolu Yonetmeligi, 2005 tarih ve 25831 sayili Resmi Gazete, 31 Mayis, Ankara, Turkey (2005) (in Turkish).
36. D. Child, The Esential of Factor Analiysis: Hold, Rinehart and Winston Ltd., London, p. 107 (1970).
37. L. Boruvka, O. Vacek and J. Jehlicka, *Geoderma*, **128**, 289 (2005).
38. R.W. LeMaitre, Numerical Petrology, Elsevier Scientific Publishing Company, Amsterdam (1982).