



INVESTIGATION OF HEAVY METAL CONTENT IN BEACH SEDIMENTS ON THE OF TASUCU BAY (MERSİN) WITH GEOCHEMICAL AND MULTIVARIATE STATISTICAL APPROACHES

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Keywords

*Heavy Metals,
Multivariate Statistical
Analysis,
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Tasucu Bay*

Abstract

The purpose of this study is to investigate the heavy metal concentration and their possible origin in recent sediments collected from 33 locations along the Tasucu Bay (Mersin) coast, Turkey. Sediment texture, major (Fe, Mg, Al, Si, Ca, Na, K, Ti) and trace elements (Pb, Zn, Mn, Sn, As, Sb, Co, Cr, Cu, Hg, Ag, Cd, Ni, Mo, V, W) in all samples were measured. The overall concentration of major and trace elements were normalized to the Al and the enrichment factor were also derived. Multivariate statistical analyses indicates significant correlation among the heavy metal fractions suggesting that the close relationship of trace metals are from the same source in the study area. The distribution of major and trace elements indicate three different factors where the first factor indicates the anthropogenic activities, the second factor indicates the natural process and the third one as intermediate factor suggesting a perfect difference between sources (anthropogenic) in the study area. Comparison of the elements with other fields shows that Sb, Mo, As, Cr, W, Ni, Sn and Co are rich. Remedial measures should be taken to restore normal conditions especially at The coastal sediments of Tasucu bay.

TAŞUCU KÖRFEZİNDE (MERSİN) SAHİL SEDİMANLARINDA AĞIR METAL İÇERİĞİNİN JEOKİMYASAL VE ÇOK DEĞİŞKENLİ İSTATİSTİK YAKLAŞIMLARLA İNCELENMESİ

Anahtar Kelimeler

*Ağır Metaller,
Çokdeğişkenli İstatistiksel
Analiz,
Veri Analizi,
Faktör Analizi,
Taşucu Körfezi*

Öz

Bu çalışmanın amacı, Türkiye, Taşucu Körfezi (Mersin) sahili boyunca 33 lokasyondan toplanan güncel çökeltelerde ağır metal içeriklerini ve olası kökenlerini incelemektir. Tüm örneklerdeki sedimanter dokusu, ana (Fe, Mg, Al, Si, Ca, Na, K, Ti) ve eser (Pb, Zn, Mn, Sn, As, Sb, Co, Cr, Cu, Hg, Ag, Cd, Ni, Mo, V, W) element içerikleri ölçülmüştür. Ana ve eser elementlerin genel konsantrasyonu Al'a normalize edildi ve zenginleştirme faktörü hesaplanmıştır. Çok değişkenli istatistiksel analizler, ağır metal içerikleri arasında anlamlı bir korelasyon ilişkisini göstermesi ve eser metallerin yakın ilişkisinin olduğunu göstermesi bunların aynı kaynaktan olduğunu göstermektedir. Ana ve eser elementlerin dağılımı üç farklı faktöre işaret etmektedir; birinci faktör antropojenik aktiviteleri, ikinci faktör doğal süreci ve üçüncüsü ise çalışma alanındaki kaynaklar arasında (antropojenik) önemli bir fark olduğunu gösteren ara faktördür. Elementlerin diğer alanlarla karşılaştırılması neticesinde Sb, Mo, As, Cr, W, Ni, Sn ve Co'nun zengin olduğu gözlenmiştir. Taşucu körfezinin özellikle kıyı çökellerinde normal koşulların yeniden sağlanması için iyileştirici önlemler alınmalıdır.

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1. Introduction

Investigation of heavy metal contents in sediments and their sources are very important for solving environmental problems. The importance of heavy metal studies in environments with live and wildlife is increasing. The adsorption properties and sedimentation processes of metals mainly depend on the composition including carbonate content, level of organic matter, grain size, Fe-Mn oxyhydroxides, etc.

The chemical contents of the surface sediments on the coasts and the statistical studies related to these contents have been expanded in the last few decades due to the negative impact of heavy metals and their damage to the ecosystem. As a result, soil or sands act as integrators and amplifiers of concentration of some elements in the waters, which overlook and shipment them and play a vital role in the shallow coastal fields (Jonathan et al., 2004). Determination of chemical contents of heavy metals, multivariate statistical analysis and data analysis related to them are the most common method for the investigation of geogenic and anthropogenic sources of heavy metals in beach sands or sediments (Facchinelli et al. 2001; Boruvka et al., 2005; Jonathan et al 2011; Leventeli 2011; Santhiya et al 2011; Yalcin et al., 2013; Yalcin et al., 2016; Gutiérrez-Mosquera et al 2018; Vetricurugan et al 2019; Yalcin et al., 2019; Jonathan et al 2019; Yalcin 2020). Scientific studies on heavy metal anomalies along the coastal areas are getting popular. Some examples include environmental impact of the El Salvador copper mine on the coastal sites (Ramirez et al., 2005) and heavy metal contents and their sources in the Mondego Cape beach and dune beach of Portugal (Vidinha et al., 2006). Several authors have conducted various research in and around the present study area from Tasucu Bay coast, Turkey (ie.) stratigraphy studies (Okyar 1991; Okyar et al., 2005; Everest and Seyhan 2006; Karakaya et al., 2010); upper slope sediment of northeastern Mediterranean (Ediger et al., 2002); coastal aquifer of Mersin (Demirel, 2004); coastal environment (Burak et al., 2004); fluxes of trace (Kocak et al., 2005). In the Mediterranean region, a high concentration of heavy minerals, corresponding to about 86% of the heap sediment, is found in some rocks of ultramafic origin to the west of Antalya. (Ergin et al., 2007). The region soils of the Musali chromite deposit have Fe and Zn anomalies ranging from 10 367 to 201 785 mg g⁻¹ and from 80 to 372 mg g⁻¹, respectively. The soil samples of Silifke and Anamur have Zn and Fe anomalies varying from 6270 to 60478 mg g⁻¹ and from 707 to 5915 mg g⁻¹, respectively (Ozdemir, 2005). Previous study by Yalcin and Ilhan (2008), the study area reveal that Fe, Al, Cl, Mg, Mn, Ti, Cr and Ni were dominant heavy metals in beach and dune sediments from Kizkalesi coast (Mersin). In Susanoglu coast (Tasucu, Mersin), Co, Cr, Mo, Hg, Cd, and Ni anomalies are greater than national acceptable values and some heavy metals show toxic anomalies (Yalcin 2008).

However, other studies have tried to distinguish the distribution areas of heavy minerals and the bedrock associated with them (Okay and Ergun, 2005). The Tasucu Bay (Mersin) in Turkey has a special importance in marine commercial activities within Mediterranean countries. In addition, the study area is also filled with calm beaches and summer residences justifying the value of the present scientific work reporting the data on geochemical elements in the beach area as it serve as basic data for comparison with future similar scientific studies.

2. Experimental**2.1. Study Area**

Tasucu is a district in the Silifke town of Mersin city and its geopolitical position, climate and landscape have attracted people since early epochs. Agriculture, trading, fishing and tourism (culture, beach, plateau and nature) are very common in the Tasucu district which was established in the Mediterranean Sea southern part of the Taurid Mountains (Fig. 1).

The Mersin harbour mainly functions as a base for commercial products and in addition it also serves for vast number of passenger vessels and motor vehicles. Orange, tangerine, lemon and strawberry are the main agricultural products that are exported from the study area. During the May-August period every year the Chelonia

Mydas and Logger Head (*Caretta Caretta*) turtles visit the Tasucu shoreline signifying the environmental importance of the study area. Tourists visit the beaches regularly between April and October for swimming and to enjoy the natural beauty where various bird species also visits during different times. The Tasucu Bay and its surroundings the Göksu delta has sunshine for a maximum of 300 days covering an area of 22,640 hectares where it hosts 332 different bird species. Göksu delta has an international importance with its watery habitat that is Convention on Wetlands of International Importance especially named as Waterfowl Habitat-RAMSAR (Tasucu Municipality, 2005).

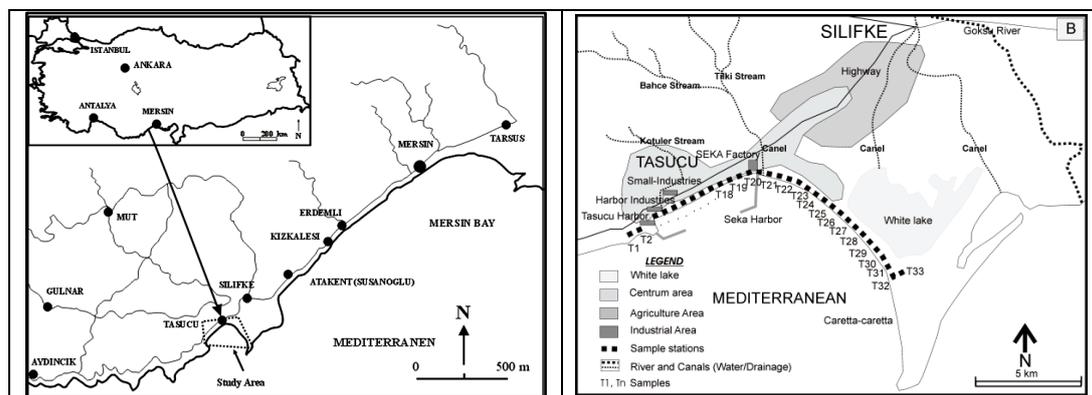


Figure 1. Study area (A) and sampling (B) locations of Tasucu beach area, Turkey.

There are old and new industries in the region that can generate harmful waste. In addition, a major harbor and human activities have altered the ecosystem prominently. Agriculture lies 10 to 20 km from the coast. Harbor industries on their hands coastal zone. The old paper factory (SEKA) is in the central coastal. Small or medium-sized industries developed in the study area near the coastline (Fig 1).

2.2. Regional geology

Mesozoic lithological units in Anatolia document the development of a mosaic of micro-continents and carbonate platforms separated by ophiolitic suture regions. Also, the area is typical of the oceanic crust formed as a result of the Triassic disintegration of Gondwana lands (Özer et al., 2004). This complex and intertwined structure was formed as a result of the closure of different branches of the Neo-Tethys Ocean (Şengor and Yılmaz, 1981; Şengor, 1987). The study area subject to study consists of sedimentary rocks and represents the Miocene carbonate rocks of the Tauride belt (Ozgul 1971, 1976). The formations in the study area were exposed in the terrestrial conditions that occurred at the beginning of the Miocene period and were deposited under sea conditions in the later geological periods (Gedik et al., 1979).

2.3. Sampling and chemical analyses

Sediment or sand samples were systematically collected along the shore using plastic shovels. Samples taken from Tasucu Bay were analyzed for sediment texture, principal and trace metals. The analyzes and method were made in accordance with the previous scientific studies (Yalcin and Ilhan 2008; Yalcin 2009). Major and trace metals analyzed using Spectro- Xepos Benchtop X-Ray Fluorescence Spectrometer (XRF). Textural studies on the sediments were performed for sand and mud distributions (Ingram 1970).

Sediment samples along the beach area in Tasucu Bay was conducted during August, 2006 and 33 systematic samples were collected from at a depth of 0-10 cm (Fig 1). Approximately 1 kg of sediment sample were collected in an equal distance interval of about 250 m with a hard plastic sample shovel. In order to minimize the contamination, the plastic bags were pre-cleaned with 6 M HNO₃ and rinsed with distilled water and then heated at 40°C before the storing the samples. Sediment samples were dried at 50°C for 24 hours and it was processed for further analysis. Dried samples were sieved through 2 mm plastic sieve and coarse grained sediments were separated. The samples were then homogenized with an agate mortar to a grain size of less than 2 mm. The mortar was washed with 6 mol l⁻¹ HNO₃ and rinsed with distilled water and dried before the each sample process.

Analyses of Cu, Al, Fe, Ag, W, Mg, Co, Ni, Zn, Mo, Sb, Hg, Ti, Cr, Cd, Pb, As, Sn, V, Si, Ca, S, Na, K and Mn element contents were obtained with the XRF. Prior to analysis, all the samples were transformed to double sided film tablets in 32 mm diameter. The detection arrangement for analysis is a Peltier cooled drift detector with energy resolution FWHM <170 eV with microprocessor controlled detectors and electronics, 10,000 pulsed input number votes were measured for the Mn and K α line. The analysis results with XRF are given as $\mu\text{g g}^{-1}$ and percentage.

BCSS1, an approved reference material, was used for analytical precision (Table 1) (Yoshinaga et al. 1996). Heavy metal enrichments were confirmed the Espinho to Mondego Cape –Portugal (Vidinha et al., 2006), Acceptable limit for Turkey (Anonymous, 2005), Kizkalesi Coast (Yalcin and Ilhan, 2008), Bosphorus (Güven et al., 1993), Eastern Black Sea (Ergül et al., 2008) and Susanoglu Coast (Yalcin 2008) by concentrations of heavy metals.

Table 1. Comparison of BCSS-1 (Yoshinaga et al. 1996) international standard values with that of present study

Elements	This Study	BCSS-1a
S(%)	1183	-
Si(%)	9.45	30.9b
Al(%)	0.53	6.26 b
Fe(%)	0.59	3.29 b
Ca(%)	22.66	0.543 b
Mg(%)	1.31	1.47 b
Na(%)	0.23	2.02 b
K(%)	0.22	1.80 b
Ti(%)	0.08	0.440 b
Mn	230.42	229
Cr	349.61	123
Cu	7.50	18.5
Ni	99.09	55.3
Co	19.18	11.4
Pb	3.39	22.7
Zn	13.52	119
Cd	4.45	0.25
As	18.41	-
Ag	3.99	-
Hg	2.34	0.129
Mo	25.16	-
Sb	5.81	-
Sn	7.91	-
V	49.13	93.4
W	7.19	-

Major Element (%), Trace metals ($\mu\text{g g}^{-1}$); a: Certified value from NRCC; b: Converted from the original certified value of the metal oxide form.

The concentration of samples were concurrently processed in statistical software [Bridgman, 1992; STATISTICA (Version 7.0)] to identify the relationship between various parameters. The whole data set was processed for three different p values ($p < 0.05, 0.01, 0.001$) to identify the maximum correlation (Davis, 1986). The standardized data set was used to generate the R-mode factor analysis [Factor 1 (F1), Factor 2 (F2), Factor 3 (F3)] with rotation was applied and the final results were also selected based on the eigen values which are more than 1. The dendograms for the results were generated from the standardized data using the formula $X - \mu - \sigma - 1$ (where σ = standard deviation; μ = mean and X = variable).

3. Results and discussion

3.1. Geochemical variations of elements

Results of textural parameters (sand, mud), sedimentary sulphur (S) and geochemical elements (Cr, Cu, Al, Pb, Zn, Fe, Mg, Ti, Sn, Mn, Ni, Co, Cd, As, Hg, Ag, Sb, W, V, Si, Ca, Na and K) collected along the Tasucu Bay shoreline is presented as Al normalized values in Table 2 and 3 respectively. The natural mineralogical variation and granular variability are best compensated by geochemical normalization, especially of major and trace elements (Loring, 1991). The Al element remains the most successful and widely used normalizer by scientists. Aluminum represents the quality of alumino-silicate, the most important carrier for metals adsorbed in beach sediments. Because, it compensates for differences in grain size and composition in the sediments. The variability of the normalized concentrations is expressed as an enrichment factors (EFs), which is a ratio of the content of the element in the analyzed layer to the content corresponding to the pre-industrial period. It is calculated by the following formula 1 :

$$EF \text{ (enrichment factors)} = (C_x/C_{Al})_s / (C_x/C_{Al})_c \quad (1)$$

where, $(C_x/C_{Al})_s$ ratio of concentration of element x and aluminium in the sample, $(C_x/C_{Al})_c$ ratio of concentration

of element x and aluminium in unpolluted sediments (Continental crustal values, Taylor and McLennan, 1985). An enrichment factor of around 1.0 indicates that the precipitate is predominantly due to lithogenic material. However, an enrichment factor much greater than 1.0 indicates that the element is mostly of anthropogenic origin (Szefer *et al.*, 1996). Thus the whole aspect in the present study is based on the geochemical interpretation of the normalized values and the enrichment order of metals in the study area.

Table 2. Results of textural parameters, sedimentary sulphate, and Al from Tasucu Bay area, Turkey.

Element/ Sample Nos.	Sand	Mud	S	Al
T1	94	6	604	0.78
T2	91	9	851	0.67
T3	93	7	1175	1.08
T4	91	9	830	0.54
T5	93	7	713	0.33
T6	93	7	4717	0.63
T7	94	6	1319	0.68
T8	95	5	953	0.44
T9	94	6	2450	0.30
T10	97	3	1764	0.31
T11	96	4	427	0.56
T12	96	4	616	0.56
T13	93	7	1321	0.49
T14	98	2	2079	0.52
T15	95	5	2726	0.36
T16	98	2	1243	0.51
T17	98	2	528	0.68
T18	96	4	2071	0.16
T19	97	3	531	0.84
T20	98	2	974	0.65
T21	98	2	1359	0.49
T22	99	1	1294	0.46
T23	98	2	1208	0.42
T24	98	2	979	0.62
T25	97	3	831	0.49
T26	98	2	836	0.42
T27	98	2	791	0.45
T28	97	3	808	0.53
T29	97	3	985	0.54
T30	97	2	431	0.64
T31	97	3	793	0.56
T32	97	3	842	0.67
T33	90	10	NA	NA
Avg.	95.79	4	1220	0.54

(All values are expressed in %)

Table 3. Al normalized values of major and trace elements from Tasucu Bay area, Turkey.

Element/ Sample No.	Si/Al (%)	Fe/Al (%)	Ca/Al (%)	Mg/Al (%)	Na/Al (%)	K/Al (%)	Ti/Al (%)	Cr/Al ($\times 10^{-4}$)	Cu/Al ($\times 10^{-4}$)	Ni/Al ($\times 10^{-4}$)	Co/Al ($\times 10^{-4}$)	Pb/Al ($\times 10^{-4}$)	Zn/Al ($\times 10^{-4}$)	Cd/Al ($\times 10^{-4}$)	As/Al ($\times 10^{-4}$)	Ag/Al ($\times 10^{-4}$)	Hg/Al ($\times 10^{-4}$)	Mo/Al ($\times 10^{-4}$)	Sb/Al ($\times 10^{-4}$)	Sn/Al ($\times 10^{-4}$)	V/Al ($\times 10^{-4}$)	W/Al ($\times 10^{-4}$)
T1	17.81	0.81	28.64	1.48	0.10	0.43	0.13	802.25	14.63	136.19	25.67	4.11	15.15	5.65	25.67	5.52	3.08	34.66	7.19	10.01	67.26	9.50
T2	20.80	0.93	32.49	1.64	0.40	0.44	0.15	898.19	16.38	138.08	28.30	5.06	18.92	6.70	29.49	4.47	3.43	37.24	9.24	11.77	79.24	10.28
T3	10.43	0.79	14.36	1.40	0.13	0.37	0.17	245.54	12.37	69.11	18.60	6.14	18.14	4.46	11.81	4.00	1.86	21.39	5.49	7.81	90.22	5.86
T4	17.47	1.08	48.87	3.20	0.15	0.39	0.15	780.43	6.35	123.23	35.47	9.15	27.45	8.40	34.91	6.35	4.85	48.54	12.14	15.31	103.44	13.82
T5	20.31	1.61	80.12	3.10	0.26	0.38	0.23	1357.39	8.16	104.00	57.44	18.14	35.98	15.72	56.84	11.79	7.86	78.60	19.05	26.30	149.95	20.86
T6	12.84	0.91	33.32	2.13	0.46	0.43	0.17	194.56	9.02	75.45	30.05	8.54	21.67	7.91	28.00	5.85	3.80	41.13	9.17	12.34	79.09	11.07
T7	16.14	0.91	30.79	2.36	0.66	0.37	0.13	687.35	33.05	140.99	27.91	12.48	36.86	6.46	27.61	5.14	3.23	36.72	8.22	10.72	84.16	10.13
T8	23.31	1.09	57.58	2.35	0.25	0.49	0.16	1772.80	16.70	202.21	41.17	6.63	48.72	9.38	50.32	8.46	5.49	61.76	12.58	16.47	101.79	16.93
T9	32.60	1.33	79.91	3.47	1.75	0.52	0.16	1086.77	9.58	317.44	56.16	8.26	37.99	14.53	67.06	12.88	8.26	89.19	18.83	25.10	131.47	24.44
T10	20.40	1.35	90.29	3.35	1.09	0.43	0.18	2308.09	107.65	173.59	58.19	9.05	24.57	15.19	75.64	19.07	8.40	84.05	21.01	29.09	192.34	25.21
T11	26.64	1.06	32.42	1.16	0.15	0.55	0.15	788.24	23.18	216.86	33.17	8.74	27.11	7.85	27.82	5.71	3.39	41.02	10.52	12.66	77.04	11.24
T12	23.87	1.01	35.75	1.21	0.27	0.56	0.14	676.66	20.05	219.83	30.07	8.23	23.81	7.88	28.82	6.27	3.58	42.96	10.02	14.14	49.94	11.99
T13	22.44	0.96	52.05	2.19	0.71	0.48	0.14	975.14	15.00	237.81	36.49	5.07	17.84	8.72	39.53	11.35	5.07	56.77	11.56	16.83	72.38	15.61
T14	20.04	0.96	47.81	2.40	0.89	0.44	0.13	669.49	14.13	207.81	36.76	4.84	15.29	7.74	42.57	6.00	4.84	52.24	12.00	15.67	93.26	14.51
T15	21.64	1.15	67.34	2.62	1.76	0.48	0.16	524.09	9.93	149.23	46.89	6.90	21.24	12.69	51.03	17.65	6.90	71.72	15.17	20.69	89.09	20.41
T16	22.49	1.09	42.50	2.10	0.84	0.49	0.14	1258.98	23.16	231.41	35.63	6.53	38.01	8.31	33.06	7.13	4.35	47.51	11.48	15.04	87.69	13.26
T17	23.86	0.97	27.29	1.10	0.28	0.48	0.14	1163.99	21.93	178.94	29.28	7.36	27.22	6.33	20.60	5.15	3.09	33.85	8.09	11.77	74.90	9.86
T18	28.11	2.23	172.93	3.43	2.78	0.48	0.20	1364.85	21.94	147.45	97.49	17.06	30.47	31.07	138.92	22.54	17.06	158.42	39.00	51.79	221.79	44.48
T19	14.33	0.97	27.29	1.16	0.10	0.37	0.15	717.43	9.83	137.45	26.52	5.45	19.06	5.21	12.19	4.62	2.60	33.15	6.63	10.30	57.54	8.29
T20	16.01	0.91	33.23	1.42	0.20	0.42	0.15	403.29	9.24	89.59	27.71	5.85	18.78	6.31	18.01	9.39	3.39	38.48	8.93	13.24	81.27	9.85
T21	17.60	1.51	45.02	3.58	0.80	0.43	0.14	195.43	6.79	265.99	43.20	5.55	32.30	9.46	49.37	9.87	4.94	51.43	12.14	14.40	123.84	15.63
T22	16.27	1.40	52.86	3.83	0.55	0.42	0.13	228.10	7.68	236.43	43.86	5.26	28.95	10.75	45.18	8.33	5.70	57.02	12.72	18.20	135.54	16.67
T23	16.62	1.44	58.59	3.15	0.53	0.42	0.15	559.84	12.81	208.99	45.07	4.98	31.55	11.39	46.26	12.57	5.93	61.68	14.71	18.74	110.78	18.27
T24	14.08	0.97	40.49	3.54	0.48	0.38	0.12	176.96	5.63	131.60	32.17	3.70	22.52	6.76	32.17	6.11	4.18	40.22	9.33	12.55	90.73	11.90
T25	15.28	1.30	49.91	3.30	0.16	0.40	0.14	347.58	6.87	191.37	40.42	4.85	24.05	9.50	40.62	7.88	5.05	50.52	12.93	16.97	103.87	15.16
T26	17.73	1.67	57.31	3.66	0.20	0.44	0.14	212.70	8.04	255.95	49.63	4.96	30.25	11.34	51.52	9.22	5.91	59.08	13.71	20.80	153.14	18.91
T27	16.02	1.32	55.46	3.57	0.18	0.41	0.14	332.53	7.71	166.26	44.04	4.18	25.99	10.57	39.42	8.15	5.51	55.05	14.31	20.04	106.81	16.30
T28	14.70	1.20	48.52	3.25	0.27	0.37	0.13	425.98	6.44	153.35	37.87	4.92	22.91	8.71	37.68	6.44	5.11	53.01	12.31	16.28	108.10	14.01
T29	16.02	1.40	40.76	3.63	0.45	0.42	0.15	740.60	8.70	241.62	38.88	6.67	29.99	8.52	40.18	7.41	4.44	44.44	11.29	15.00	71.47	14.44
T30	15.56	1.11	39.65	3.34	0.13	0.38	0.14	517.02	5.33	158.40	32.90	3.13	21.93	5.95	35.88	7.36	4.07	42.30	9.24	11.59	80.69	11.91
T31	14.92	1.18	43.58	2.99	0.50	0.39	0.14	398.63	5.90	167.67	35.75	5.01	37.72	7.51	29.32	6.79	4.29	48.26	10.37	14.84	79.37	12.87
T32	15.14	1.19	34.31	3.69	0.29	0.38	0.12	323.61	6.26	185.37	32.81	2.98	24.16	7.01	34.60	5.52	3.58	40.26	9.54	12.23	88.28	11.33
T33	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

All elements were normalized to aluminum to gain a deeper insight into the mechanisms underlying the different areas of the coast and therefore the origin of the sediments (e.g. Calvert *et al.*, 1993). This element can be considered to represent the detritic component best, as it is assumed to be present only in aluminum silicate phases, along with quartz, which are typical minerals forming the basin under investigation (Careda *et al.*, 1999). The trend of the Fe/Al and Mg/Al ratio (Table 3) generally suggest that mostly all the sediments in the beach is supplied through anthropogenic sources and partially through natural sources (in some stations) as the study area lies in a curve like structure. However, the trend of the Fe/Al indicates that it not only receives material deriving from the normal erosion/deposition processes in T1-T3, T6, T7, T13, T14, T17, T19, T20 and T24 of stations. The trend of the Mg/Al ratio (Table 3) generally reveals that the beach sediments is also supplied by different sources in T4, T5, T9, T10, T18, T21-T30 and T32 stations. The distribution of trace element such as Ti and Al is constant, and it could be inferred that the material is brought down by the rivers (Goksu River, Water/Drainage canals, Kotuler, Bahce and Tilki Streams) close to the area affecting the composition of the sediment which are primarily from the Miocene carbonate rocks (Fig 1). The K/Al ratio (Table 3) is generally constant along on the coast and reflects the distribution of the potassium feldspars present in the host carbonate rocks.

The low variations in certain major (Na, Si, Ti and K) and trace element (Pb, Cu, Cd, Ag and Hg) concentrations (Al normalized values) suggests that the bulk mineral composition is from the same source. However, the concentration pattern of Ca is very high (14.36%-172.93% concentration range) compared to other major elements indicating that the area is dominated by carbonate rocks. The marked increase of trace metals in the beach sediments matches the industrial revolution during the last two decades suggesting that the anthropogenic activities has increased in this part of the area. The region's economy (Tasucu Bay) is mostly based on sea-related activities, shipbuilding, automobile industries, agriculture, chromite mining are some of the highlights among the industrial activities. The geographical position in the present study is most important in explaining the differences observed among the sediments. The higher concentrations of trace metals in the central part is mainly due to the (shipbuilding activities, the old SEKA Factory and endustrial activities) indicating that the source area is dominated by these industries. The higher values of trace metals (Cr, Cu, Pb, Zn, Cd, Hg, As, Mo, Ag, Sn, Sb, W) in the present study indicates that the increase in input of metals from the intertidal activities of the beach area and they are from a multiple source points in the study area.

3.2. Correlation matrix

Correlation matrix of the geochemical parameters in the present study indicates distinctive relationship among major and trace elements (Table 4). The positive relationship (> 0.50) among sand vs contaminated elements (Sn, Ag, Hg, As, Sb, Mo, W) indicates that these trace elements are attached to the surface of sand particles. Moreover, the positive association of these elements with Fe indicates that they could be from the effluents of iron related industries. The association of Ca and Mg with these elements (Sb, As, Hg, Ag, Mo, W, Sn,) also suggests that they are absorbed onto the calcareous materials in the beach sediments rather than the finer sediments. The above inference on association of elements clearly signify that they are anthropogenic in nature. The enrichment of trace metals in the beach sediments is mainly due to the anthropogenic sources which includes waste from heavy metal-bearing fuel industries, chemical clean-up material of vessels at the Tasucu harbor, chemical and product wastes of the old SEKA paper plant at the harbor, urban wastes of Tasucu town and wastes of fertilizers used in the agricultural fields. All along the coast there is no strong currents which will significantly affect the beach, but the small waves generated in the coast and Tasucu harbor could affect the deposition of sediments in the beach region. The enrichment of metals in samples (T19, T20, T21) could also be due to the impact of vessel wastes on the Tasucu coast. The negative impact of chemical material wastes is observed in samples collected in the vicinity of the old SEKA paper plant. Similarly, fertilizer contamination is also detected in areas of river outlets, uncontrolled urban wastes, waste disposal sites of hotels on the coast and recent coastal erosion.

Table 4. Correlation coefficient matrix (R2) of major and trace elements in recent sediments from Tasucu beach area, Turkey (p <0.05*, 0.01†, 0.001‡)

	Sand	Mud	S	Si	Al	Fe	Ca	Mg	Na	K	Ti	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd	As	Ag	Hg	Mo	Sb	Sn	V	W
Sand	1.00																										
Mud	-	1.00																									
S	-	-	1.00																								
Si	-	-	-	1.00																							
Al	-	-	-	0.71*‡‡	1.00																						
Fe	0.41*	-	-	0.52*†	0.81*‡‡	1.00																					
Ca	0.40*	-	-	-	-	-	1.00																				
Mg	0.35*	-	-	-	0.40*	0.67*†‡	0.43*	1.00																			
Na	-	-	0.65*†‡	-	-	-	-	-	1.00																		
K	-	-	-	0.87*†‡	0.94*‡‡	0.72*†‡	-	-	-	1.00																	
Ti	-	-	-	0.64*†‡	0.95*‡‡	0.74*†‡	-	-	-	0.88*†‡	1.00																
Mn	0.40*	-	-	0.75*†‡	0.64*‡‡	0.73*†‡	0.40*	0.43*	-	0.73*†‡	0.55*†	1.00															
Cr	-	-	-	0.60*†‡	-	-	-	-	-	0.35*	-	-	1.00														
Cu	-	-	-	0.35*	-	-	-	-	-	-	-	-	0.62*†‡	1.00													
Ni	-	-	-0.43*	-	-	-	-0.82*†‡	-	-	-	-	-	-	-	1.00												
Co	0.40*	-	-	0.60*†‡	0.85*†‡	0.83*†‡	-	0.73*†‡	-0.36*†‡	0.43*	0.48*†	0.54*†	-	-	-	1.00											
Pb	-	-	-	0.47*†	0.53*†	0.34*	-	-	-	0.52*†	0.65*†‡	-	0.36*	0.45*†	-0.35*	-	1.00										
Zn	-	-	-	0.54*†	0.64*†‡	0.67*†‡	-	-	-	0.61*†‡	0.60*†‡	0.56*†‡	-	-	-	0.46*†	0.58*†‡	1.00									
Cd	-	-	0.37*	-	-	0.47*†	0.66*†‡	-	-	-	-	-	-	-	0.78*†‡	-	-	-	1.00								
As	0.34*	-	-	-	-	-	0.81*†‡	0.56*†‡	0.36*†‡	-	-	0.38*	-	-	-	-	-	-	0.58*†‡	1.00							
Ag	-	-	-	-	-	-	0.55*†‡	-	-	-	-	-	-	-	0.58*†‡	-	-	-	0.40*	0.39*	1.00						
Hg	0.40*	-	-	-	-	0.43*	0.97*†‡	0.54*†	-	-	-	0.45*†	-	-	0.85*†‡	-	-	-	0.74*†‡	0.84*†‡	0.55*†‡	1.00					
Mo	0.35*	-	-	0.38*	0.36*	0.52*†	0.91*†‡	0.47*†	-	-	-	0.58*†‡	-	-	0.79*†‡	-	-	-	0.64*†‡	0.72*†‡	0.56*†‡	0.92*†‡	1.00				
Sb	0.40*	-	-	0.35*	0.35*	0.59*†‡	0.86*†‡	0.51*†	-	-	0.35*	0.60*†‡	-	-	0.85*†‡	0.35*	-	-	0.80*†‡	0.75*†‡	0.47*†‡	0.90*†‡	0.86*†‡	1.00			
Sn	0.43*	-	-	-	0.38*	0.58*†‡	0.81*†‡	0.39*	-	-	0.40*	0.52*†	-	-	0.82*†‡	0.37*	-	-	0.78*†‡	0.54*†	0.51*†	0.81*†‡	0.90*†‡	0.81*†‡	0.90*†‡	1.00	
V	-	-	-	-	0.66*†‡	0.73*†‡	-	0.57*†‡	-	0.52*†	0.69*†‡	0.40*	-	-	0.51*†	0.57*†‡	0.38*	0.49*†	0.54*†	0.36*	-	0.47*†	0.45*†	0.59*†‡	0.59*†‡	1.00	
W	0.42*	-	-	-	-	-	0.80*†‡	0.61*†‡	-	-	-	-	-	-	0.45*†	0.38*	-	-	0.50*†	0.86*†‡	0.47*†	0.81*†‡	0.71*†‡	0.63*†‡	0.57*†‡	1.00	

The close association of Al vs K (0.94) clearly indicates the presence of potash feldspar in the beach sediments. The association of Si vs Al (0.71), Fe (0.52), K (0.87), Ti (0.64), Mn (0.75) suggests that they are present as aluminosilicates in the beach sediments. The positive relationship of Si vs Cr (0.60), Pb (0.47), Zn (0.54) clearly suggest that they are from external source and are bound in the outer side of the sandy particles. Terra rossa soils characteristically observed in southern parts of the Bolkar Dağları Mountains comprise the source of Al. The positive relationship of Fe with K, Ti indicates the deposition of sediments from the basement rocks that the Bolkar Dağı unit as it is represented by carbonate and clastic rocks together with olistostrome rocks with ages changing from Devonian to lower Tertiary. The Bozkır unit is composed acidic tuff, basic, ultrabasic rocks and serpentinites and also shelf units and oceanic crust rocks of Triassic-Senonian age that were formed in various facies and environments (Yetis and Demirkol, 1986; Ozgul and Kozlu, 2002). The association of Ca, Mg with toxic elements (Ag, Hg, Cd, Sb, Sn, As, Mo, and W) clearly signifies that they are absorbed into the calcareous materials in the beach sediments. The association of Cr vs Cu (0.62); Pb vs Zn (0.58); Cd vs As (0.58), Hg (0.74) Mo (0.64), Sb (0.80), Sn (0.78), V (0.54), W (0.50) indicates that they are anthropogenic which is mainly due to the effluent or industrial input in the study area. The association of trace metals (Sb, As, Mo, Ag, Hg, Sn) among themselves suggest that they are from a single source closely related to chemical industry.

3.3. Factor and cluster analysis

Three factors were derived based on the eigenvalues (> 1) as well as the total variance to determine the factors with different characteristics that control the distribution of different variables in the beach area. The overall systematic variation in the factor analysis is presented in Figure 2, Table 5.

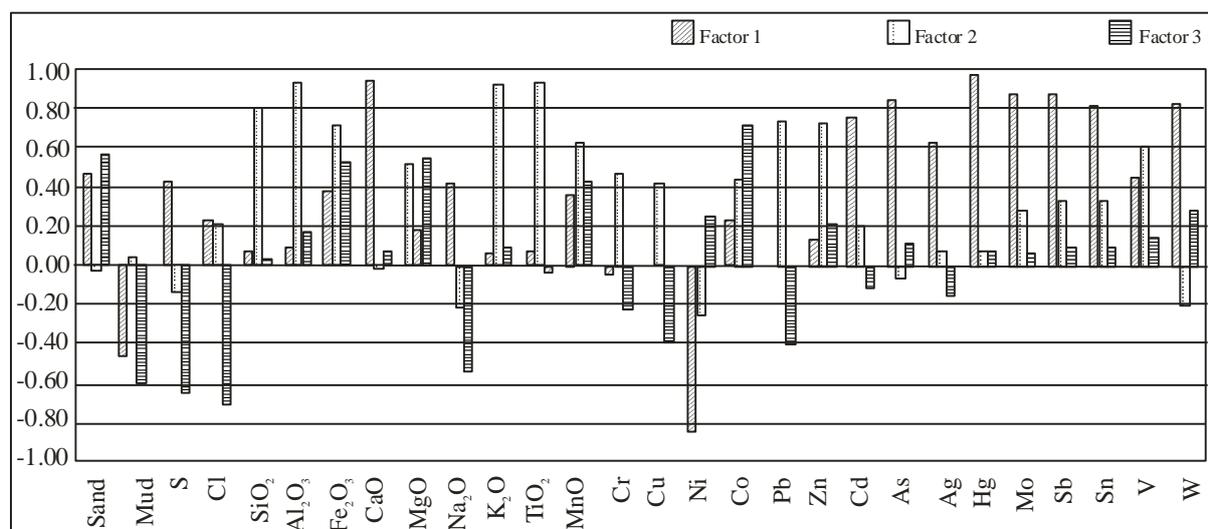


Figure 2. Results of factor analysis (R-mode) showing the relationship between the various elemental compositions of the three primary factors in surface sediments of Tasucu beach area, Turkey.

Table 5. Explanation of cumulative percentage of sediment samples with eigen values

Factor	Eigen values	Cummulative percentage
1	10.52	37.57
2	5.31	56.54
3	3.49	69.01

The first factor has a high eigenvalue of 10.52, and this value explains 37.57% of the total variance. In the first factor, the association of Ca, Mg, Cd, As, Ag, Hg, Mo, Sb, Sn and W point out that they are associated with the calcareous rocks found of the study area (Ca and Mg) in the beach sediments. The general distribution of heavy metals is similar to the anomalies of Susanoglu beach sands (Yalcin 2009). In addition, all the elements apart from these are polluted elements and it is not from a natural source. In this case, the factor belonging to these elements can be named as "anthropogenic factor". The second factor (Factor 2) explains 18.92% of the total variance with an eigenvalue of 5.31. This factor can be termed as "natural process factor" where it is clearly identified by the association of Si, Al, Fe, K, Ti, V and Mn. The unity of the above elements is important. Because these also indicate the presence of heavy minerals in beach sediments. The association of Zn and Pb with these elements explains that they are anthropogenic and show that they are together with heavy metals in the study area. The third factor (Factor 3) explains 12.47% of total variance with an eigenvalue of 3.49. This factor can be termed as "intermediate factor" indicating the association of sand, Fe, Mg and Co. The separate behavior of Co in this factor indicates that it is from a separate origin than other elements and also with Fe related industries. Iron-bearing wastes from

maintenance of vessels at the Tasucu harbor might be the source of pollution. In addition, small-scale trash and industrial wastes can also cause these type of association.

Cluster analysis made out of complete linkage analysis indicates four different clusters which are clearly marked as cluster 1, 2, 3 and 4 (Fig 3). The analysis of cluster analysis indicates that Ni has a separate source in the Tasucu and it is closely associated with the finer sediments (Cluster 1). The close linkage of W, As, Cd, Sn, Sb, Mo, Hg with Ca suggest that they are with the carbonate fraction and where the sulphates are also high as evidenced in cluster 2. The linkage of Pb, Cu, Cr, Zn, K, Ti, Al, Mn, Si suggest that these elements are in the form of aluminium silicates and/or ultrabasic rocks and the separate linkage of Pb, Cu, Cr indicates that they are of separate origin from a different source (Cluster 3). The clustering of V, Mg, Co, Fe with sand in cluster 4 reveals that the trace metals are combined with the sand fraction especially as coatings along with Fe and this could be closely related to the iron related smelting industries. The observed linkage distance between various parameters in the cluster analysis suggest that the source area for these elements are from various sources of different industries.

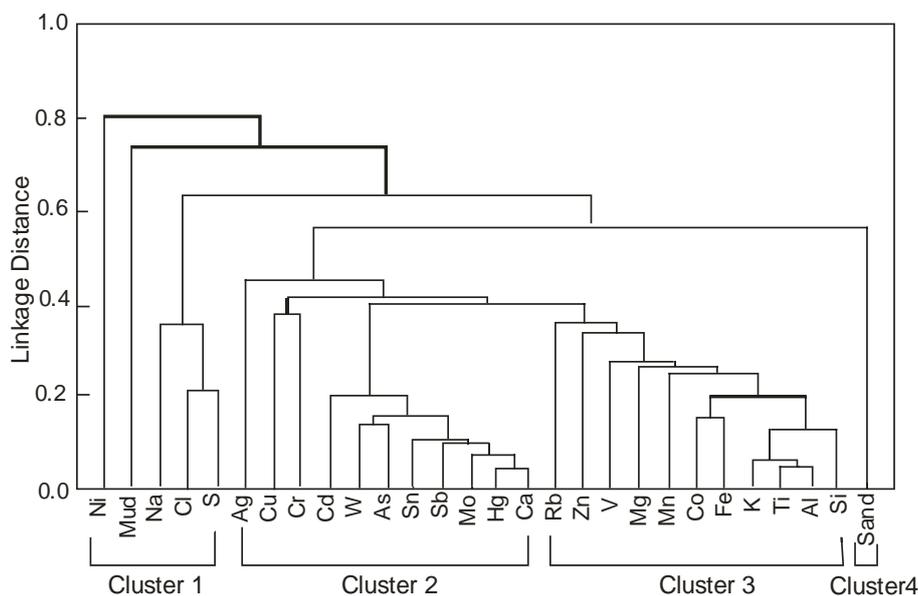


Figure 3. Dendograms based on complete linkage method for samples of Tasucu beach area, Turkey

4. Evaluation of metal pollution

The enrichment of trace metals were evaluated based on the enrichment factor calculations (EFs). Normally the higher EF values of more than 1 indicates that the concentration of elements are high than the normal level (Zoller *et al.* 1974; Hakanson, 1980). The enrichment order of the trace metals indicates the following order: Sb (501.14)> Mo (286.87)> As (218.10)> Cr (70.03)> W (60.93)> Ni (32.32)> Sn (24.61)> Co (18.56)> V (7.60)> Cu (4.93)> Pb (3.25)> Zn (3.03)> Fe (2.71)> Ag (1.38)> Cd (0.78). The higher EF values in the beach sediments reflects record of anthropogenic activities which are presently at very high levels in the Tasucu bay area. The EF values of present study indicates very high values which is mainly due to the low Al content in the sandy sediments. The principal sources for these contaminants includes wastes of vessels navigating over the Tasucu Bay, wastes from tourism activities, municipal wastes from settlement area of the Tasucu Bay, uncontrolled urban wastes of the Tasucu Bay, highway between Mersin and Antalya road, fertilizers used in agriculture and trash sites of touristic hotels industries situated close to the beach area and the effluent input through agricultural activities.

The enrichment pattern further suggest that the metals are first distributed into the coastal area and then they have been deposited in the beach sediments due to the tidal activity which does not the force the sediments to be transported to other areas or deep inside the coast. The higher EF values of Ca (134.12) and Mg (16.02) suggest that the contaminants are closely associated with the carbonate fractions in the study area which is also dominant with the Miocene group of rocks.

The comparison of metal concentration with other in the study area with other coastal regions indicates it is contaminated considerably by trace metals (Cr, Cd, Hg) (Table 6). The enrichment of these trace metals suggest that they are specifically supplied from the anthropogenic activities that is taking place in the region and from the surrounding industries. The higher values also indicate that certain measures (environmental management) must be made to reduce the level of the abnormal metals in sediments before they get out of control.

Table 6. Comparison of metal concentration of various elements from different parts of world and Turkey with that of Tasucu beach area, Turkey

Study area/ Elements	Portugal (1)	Acceptable limit for Turkey (2)	Kizkalesi (3)	Bosphorus (4)	Eastern Black Sea (5)	Susanoglu (6)	Present study
Al	61000	-	8267	-	-	11924.24	5300
Fe	21000	-	18803	11100-31000	56800-60500	13909.09	5900
Mg	7000	-	34993	-	-	15624.24	13100
Mn	369.8	-	586	112-146	652-673	333.85	230.42
Ti	-	-	813	-	-	736.36	800
Ag	-	-	4.13	-	-	4.12	3.99
As	-	20	24.74	-	12.60-13.10	19.91	18.41
Cr	62.8	100	554	22.04-61.71	70.02-74.24	428.06	349.61
Co	47	20	28.2	9.03-21.76	22.60-23.90	21.41	19.18
Cu	361.2	50	10.13	7.44-46.16	52.03-56.86	12.81	7.50
Cd	-	-	4.21	2.28-3.22	<0.02	4.32	4.45
Hg	-	1	2.05	-	-	1.72	2.34
Mo	-	10	25.96	-	-	27	25.16
Ni	39.9	30	186.8	16.79-58.74	23.61-26.53	145.52	99.09
Pb	71.7	50	4.55	35.7-135.3	<0.1	5.51	3.39
Sb	-	-	5.95	-	0.64-0.99	5.67	5.81
Sn	-	20	8.17	-	-	7.83	7.91
V	-	-	63.3	-	-	38.12	49.13
W	-	-	7.61	-	-	6.58	7.19
Zn	112.8	150	19.75	42.80-118.53	169-182	17.80	13.52

All values ($\mu\text{g g}^{-1}$) are expressed as (1) Vidinha *et al.* 2006; (2) Anonymous, Acceptable limit for Turkey, 2005; (3) Yalcin and Ilhan 2008; (4) Guven *et al.*, 1993; (5) Ergul *et al.*, 2008; (6) Yalcin 2008.

5. Conclusion

The overall study in the Tasucu bay area indicates that the beach sediments are sandy in nature and are partially reduced in nature due to the presence of high concentration of sulphates. The presence of carbonates in the study area suggest that the trace metals in the study area are closely associated and absorbed in the carbonates (as evidenced by correlation of elements). The close relationship and clustering of trace metals (Ag, W, As, Cd, Sn, Sb, Mo, Hg) with carbonates suggest that they are associated with the carbonates. Heavy metals (Pb, Cu, Cr, Zn, K, Ti, Al, Mn) accumulation is associated with the aluminium silicates and ultrabasic rocks. The concentration pattern and the association of Pb, Cu, Cr indicate that they are of separate origin from a different source whereas, V, Mg, Co, Fe are associated with coarse grained particles (sand) suggesting that they are closely related to iron related smelting industries.

Based on results of basic geochemical chemical analysis and statistical relationship among the elements, the trace metal distribution pattern indicates that the beach sediments are contaminated to a considerable extent which will act as possible toxic agents for environment and human health and care should be taken immediately to bring down the level of enrichment of metals.

Conflict of Interest

No conflict of interest was declared by the authors.

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