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Assessment of trace metal pollution in the coastal sediments of Fethiye-Göcek Bay (SW Turkey) and evaluation of pollution sources

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ABSTRACT

This research evaluated the trace metal pollution and the pollution sources in the coastal sediments of Fethiye-Göcek Bay by using the spatial distribution maps, correlation and statistical analysis, which were acquired from 69 sampling points. Spatial distribution maps for eleven elements (namely Al, As, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, and Zn) revealed that there is an enrichment of the studied elements, especially near Fethiye harbor. Moreover, the contamination evaluation carried out by using different evaluation methods suggests considerable contamination of As, Co, Cr and Ni. There is a high correlation between Ni, Co, and Fe, Even the minimum Ni concentrations are 9 fold enriched relative to the Earth Crust's values. The controlling factors for element distribution in the area are both natural and anthropogenic. The natural sources are related to the weathering of the geological units and hydrothermal activity. In contrast, various anthropogenic sources include coal smoke, fuel oils used near the crowded harbors, urbanization and the increase in the population recently. When the ecological risk of these enriched elements is considered, the level of probability of toxicity comes out to be the highest, which demonstrates that the accumulation of trace metals in harbor sediments should be considered in the near future to prevent any contamination toward biota and human.

1. Introduction

Understanding the sources and toxicity of trace metals in the environment is vital for environmental protection. The toxicity and longevity and non-biodegradable character of trace metals in the environment, especially in aquatic ecosystems (rivers, lakes, groundwater, and oceans) make them a persistent health threat to living organisms (Gui et al., 2017; Liu et al., 2019). There are both natural and anthropogenic sources of trace metals in such systems including atmospheric deposition of aerosols, agricultural fertilizers, livestock manures, industrial activities, urbanization, mining activities, crustal erosion, mobilization of the trace metals that are naturally present in rocks etc. (Quevauviller et al., 1989; Onodera et al., 2008; Cheng et al., 2013; Arslan, 2017; Jiang et al., 2017).

In geochemical prospecting studies, metal investigation has been used as a standard procedure for >50 years since the occurrence of mineralized deposits along the drainage area of some rivers affects the stream sediment chemistry (Hawkes and Webb, 1962; de Groot, 1995). Generally, understanding the metal contamination in aquatic environments requires an in-depth analysis of the contamination status of not only the water body itself but also the base sediments in that environment. The base sediments act as biochemical reactors and the deposited metals are involved in different processes like precipitation-dissolution, adsorption-desorption of minerals, which control metal speciation (de Groot, 1995). If there is a metal transfer from the aquatic environment to the base sediments, then these sediments become secondary pollution sources (Li et al., 2000; Hatje et al., 2002; Gaur et al., 2005; Varol and Şen, 2012; Gu et al., 2015). Metals can be released from the sediment to the overlying aquatic environment following a change in the environmental conditions (erosion and re-deposition of sediments, variation in

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pH, temperature, etc.) where adsorption-desorption mechanisms are prevalent. As a secondary pollution source, the base sediments contain almost 99 % of the charged metals (de Groot, 1995; Baalousha et al., 2019; Joksimovic et al., 2011; Dong et al., 2012; Rahman et al., 2014).

It is possible to evaluate the level of trace metal contamination in aquatic sediment systems by using many international evaluation methods, such as Geo-accumulation Index (I_{geo}), Enrichment Factor (EF), Pollution Load Index (PLI), and Potential Ecological Risk Index (RI) (Jiang et al., 2014; Gülşen-Rothmund et al., 2018; Abadi et al., 2019; Balık and Tunca, 2015; Gülşen, 2017). These evaluation methods are practical tools in distinguishing the anthropogenic metal pollution since they are based on a comparison of the current concentrations with geochemical background values (Balık and Tunca, 2015; Gülşen, 2017).

The study area, Fethiye, is located in the southwest of Turkey within the province of Muğla (Fig. 1). Fethiye is one of the districts of the Muğla province in which the main source of income is tourism. Since Fethiye is one of the most important tourism centers of Turkey, the coastal parts are especially busy with the tourism-intended activities. These activities, along with urbanization, port facilities and fishing, put an anthropogenic pressure on the coastline of the Fethiye-Göcek Bay (Bann and Başak, 2013). Turkish government declared Fethiye-Göcek Bay as a Special Environmental Protection Area in 1988 due to its natural and historical features. Two species of sea turtles (*Caretta Caretta* and *Chelonia mydas*), which are under protection according to the Bern Convention, lay their eggs on the beaches of this area. Besides, some endemic species of trees (e.g. *Liquidambar Orientalis*) are present in the

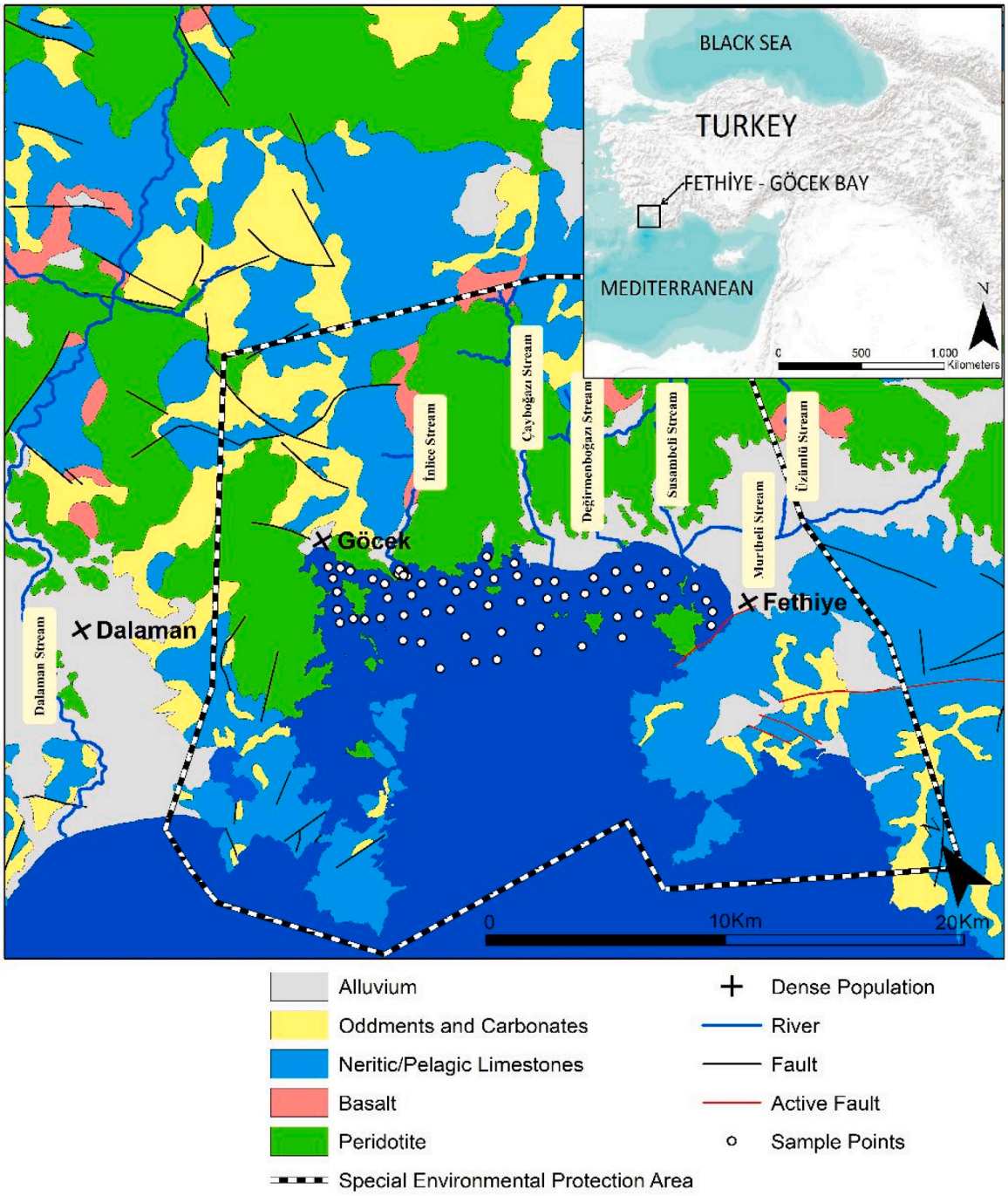


Fig. 1. Location and geological map of the study area (Taken and modified from General Directorate of Mineral Research and Exploration 1:500000 Scale Geological Inventory Map Series of Turkey Denizli Section prepared in 2002).

Fethiye area (Bann and Başak, 2013).

The sustainability of not only this unique aquatic ecosystem but also such systems around the world requires an assessment of the pollution and delineation of the pollution sources within the coastal sediments. Coastal regions are under high anthropogenic pressure induced by environmental stresses and degradation. Clean and safe ecosystems are threatened by various activities like tourism, and contamination of water, sediment and soils by trace metals (TMs) that can be transferred from one natural compartment to another. Thus, the evaluation of TMs in marine sediments is necessary to address the different issues induced. Therefore, this study assessed the TM pollution in the Fethiye-Göcek Bay, to put forward the spatial distribution of selected TMs (Al, As, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, and Zn) in the coastal sediments of Fethiye – Göcek Bay and to discuss the possible sources of these elements.

2. Study area

The study area is located in the Western Mediterranean Region of Turkey (Fig. 1). The climate of the area is a Mediterranean climate; summers are hot and dry, winters are warm and rainy. The average annual rainfall in the region is 983 mm, and the average temperature is 17.7 °C (climate-data.org). The study area is located on one of the main tectonic units of SW Anatolia, namely Lycian nappes. The other major tectonic unit of SW Anatolia, the Beydağları Autochthon is the base rock in the region and it is separated from Lycian nappes by a tectonic contact.

The Beydağları Autochthon comprises limestones and claystones. Lycian Nappes include five different units: from bottom to top, Yeşilbarak, Tavas, Bodrum, Gülbahar, and Marmaris Nappes (Şenel, 1997). These different units are not differentiated in the geological map presented in Fig. 1 for simplicity only the geologic units are presented, which include sandstones, shales, carbonate-dominated rocks, basalts, and peridotites. Quaternary alluvium units can also be observed around the Fethiye and Göcek cities. Multi-directional extension resulted in NE-SW striking active normal faults in the region (Tosun et al., 2021). İnlice, Çayboğazı, Değirmenboğazı, Susambeli and Murtbeli Streams are located between Fethiye and Göcek harbors and flow into the Mediterranean Sea (Fig. 1). Most of these streams have low flow rates today and some of them even cease to flow during summer (Koç, 2012). These surface waters are thought to have low concentrations of dissolved trace metals since their discharge rates vary with the precipitation received during the wet seasons.

3. Materials and methods

3.1. Sampling and analytical procedures

Sediment core sampling was carried out at 69 different locations in Fethiye-Göcek Bay in 2014. Sampling points were homogeneously distributed throughout the study area (Fig. 1). Previous investigations in the area (Avşar et al., 2017) revealed a subaqueous hot spring (SUB-7 in Fig. 1) which is enriched in some elements like S, Cl, Ca and Sr. To put forward the possible effects of hydrothermal activity in sediment chemistry, 10 points were sampled in the close vicinity of this hot spring (sample ID's I109, I111, I114, I120, I122, I129, I130, I131, I132, I135 in Table 1). During sampling, the gravity core method was followed in which the gravity corer was subjected to free fall about 2 m above the sea bottom. The minimum length of the sediment cores came out to be 10 cm, and approximately the top 5 cm of this length was submitted to the laboratory for Inductively- Coupled Plasma Mass Spectrometry (ICP-MS) analysis. The samples were prepared for ICP-MS analysis in the Fatsa Faculty of Marine Sciences Research and Laboratory Center (Ordu, Turkey). Before their shipment to Fatsa, the samples were kept cold at around 4 °C. During the preparation of the samples for ICP-MS analysis, the samples were oven-dried at 105 °C, homogenized with a porcelain mortar, and about 100 g of the sample was passed through a 63 μm mesh sieve (Gülşen, 2017). Part of the samples finer than 63 μm were weighed, and about 3 g of each sample was separated to be shipped to Acme Laboratories (Bureau Veritas Commodities Canada Ltd). At Acme Laboratories, samples were digested in 1:1:1 HNO_3:HCl:H_2O aqua regia (method code AQ270) and then ionized by argon plasma at 10.000 K. After this step, the ionized components were measured using a multiplexer detector in an MS machine (Thomas, 2004). The detection limits for Mo, Cu, Pb, Ni, Co and Cr are reported as 0.5 ppm; 5 ppm for Zn, Mn and As; 10 ppm for V and Ti; 0.01 % for Al and Fe.

3.2. Geostatistical procedures

In this study, Ordinary Kriging (OK) procedure was used as an interpolation method (Matheron, 1969; Webster and Oliver, 2001; Tunçay et al., 2018) to demonstrate the spatial distribution of the aforementioned elements in the study area. To create the interpolation maps, equal variogram parameters (range, nugget effect, and sill) were used. The maps were prepared using the Geostatistical Analyst tool of ArcGIS 10.2.1.

3.3. Statistical analyses

Excel Statistical software was used to conduct the Hierarchical Agglomerative Clustering (HAC) and the Principal Component Analysis (PCA) in this study. Before the analyses, bulk elemental concentrations were standardized using Z scores so that each variable would have an equal influence on the analysis. PCA is a multivariate technique by which the dimensionality of large datasets can be reduced, and important information can be extracted from the dataset (Pearson, 1901; Hotelling, 1933). In this study, we used PCA to identify the variables having a significant effect on the sediment quality and to expose the potential pollution sources. HAC is a method of cluster analysis based on developing a hierarchy of clusters. In the Cluster Analysis technique, natural clusters of resemblance in a class and variations of different classes are revealed (Lattin et al., 2003). There are two different modes of HCA. In R-mode, the clusters of variables are acquired, in Q-mode, the cluster of samples is attained (Bhuiyan et al., 2016). In this study, squared Euclidean distance was used during HCA to show the goodness of similarity. Ward's method was used (Ward, 1963), and only R-mode HCA was performed for linkage.

3.4. Sediment contamination evaluation methods

The soil or sediment contamination analysis methods compare the current state of the sediment with its state prior to the industrial age. Some of these methods even consider the effects of trace metal contamination on living organisms. These evaluation methods can be categorized into three main groups: i) the ones that expose the extend of anthropogenic pollution in the sediment, ii) the ones that rather evaluate the impact of the contamination on the ecosystem and iii) the ones that present the limit and/or reference values (Balık and Tunca, 2015). The most commonly used reference values are the ones proposed by Turekian and Wedepohl (1961). To assess the quality of the sediments collected in this study, the evaluation methods presented below were used.

3.4.1. Contamination factor (CF)

Hakanson (1980) established the contamination factor as a method to exhibit the anthropogenic metal contamination of the sediments. This technique compares the current concentration of the metal in the sediment (C_i) against a background concentration (C_n) assumed to represent the pre-industrial concentration. In this study, the average abundances reported by Turekian and Wedepohl (1961) were used as the background concentrations. CF is calculated as follows

Table 1
Trace metal concentrations in the sediment samples collected from Fethiye-Göcek Bay with the descriptive statistics of the dataset.

Sample ID	X	Y	Concentrations (units in ppm for all elements except for Al, Fe and Ti which are in %)												
			Mo	Cu	Pb	Zn	Ni	Co	Mn	As	V	Cr	Ti	Al	Fe
F1	687,939	4,055,601	1.0	32.4	23.1	94	1449.9	80.7	717	36	69	325.8	0.059	1.71	5.90
F11	683,750	4,057,461	0.6	20.9	14.9	62	934.0	53.9	576	19	62	222.2	0.044	1.40	4.09
F12	684,102	4,058,485	1.5	24.5	16.9	63	1182.4	74.2	650	23	57	271.5	0.061	1.36	4.86
F13	685,292	4,059,431	0.8	22.1	17.0	61	963.2	56.3	531	32	61	224.3	0.045	1.23	4.29
F14	685,241	4,060,507	0.7	18.6	16.3	59	922.4	50.3	491	32	58	232.1	0.044	1.19	4.22
F15	684,122	4,060,834	0.7	20.1	14.8	62	840.4	49.5	459	24	50	219.4	0.040	1.22	3.97
F16	684,254	4,059,913	0.8	20.4	16.4	61	910.9	51.7	503	29	59	227.9	0.039	1.31	4.28
F18	681,776	4,058,139	0.7	30.7	16.2	71	1207.8	75.2	815	23	53	248.6	0.056	1.83	4.86
F19	683,306	4,060,356	0.7	21.6	15.6	62	870.6	49.9	449	23	53	212.7	0.034	1.30	4.13
F2	688,363	4,056,177	0.7	32.1	19.3	92	1431.0	77.3	702	31	65	326.2	0.060	1.61	5.77
F21	682,368	4,060,784	0.6	27.1	16.1	69	847.0	53.9	536	21	54	215.3	0.033	1.54	4.25
F23	679,671	4,059,085	0.8	25.7	22.1	65	789.4	44.9	726	37	59	197.0	0.037	1.42	3.86
F24	680,482	4,060,097	0.5	19.1	15.9	51	896.9	47.7	477	19	54	187.3	0.032	1.17	3.66
F25	681,554	4,061,164	1.0	32.7	17.2	74	823.5	58.2	481	19	55	214.6	0.031	1.75	4.37
F26	682,323	4,061,719	0.6	18.4	11.1	54	775.9	50.5	474	13	39	196.9	0.032	1.16	3.73
F27	681,579	4,062,136	0.6	18.1	10.4	50	804.6	46.1	468	14	38	199.4	0.033	1.13	3.68
F29	680,862	4,062,964	0.8	21.5	12.6	59	899.7	47.3	486	17	45	209.4	0.030	1.25	3.99
F3	688,386	4,056,817	0.8	25.0	18.0	74	1329.6	77.5	665	40	67	306.4	0.060	1.52	5.67
F30	680,315	4,061,729	0.8	22.2	16.4	64	864.9	55.0	491	22	56	209.6	0.032	1.37	4.03
F33	677,723	4,059,825	0.6	23.4	21.3	67	758.7	45.0	581	26	55	193.7	0.034	1.36	3.68
F34	678,659	4,060,908	0.6	19.5	17.9	58	813.4	43.6	561	21	53	203.6	0.033	1.23	3.66
F36	679,773	4,063,445	0.7	21.3	16.3	65	990.1	57.3	516	25	49	227.0	0.030	1.24	4.20
F37	678,793	4,062,439	0.6	21.5	15.6	61	966.6	49.6	497	19	55	211.0	0.029	1.22	3.98
F38	679,251	4,064,155	0.7	21.9	16.2	66	1200.4	68.2	554	25	51	241.9	0.028	1.15	4.54
F39	678,685	4,063,745	0.5	21.3	16.7	71	1048.7	57.6	614	22	49	226.5	0.029	1.14	4.14
F4	688,268	4,057,693	0.7	29.9	17.3	84	1654.4	99.4	719	32	65	361.4	0.057	1.58	6.23
F42	676,705	4,060,313	0.9	26.9	20.8	78	728.0	44.1	1017	41	60	190.5	0.033	1.56	3.89
F44	676,980	4,061,670	0.8	27.6	19.4	66	775.0	46.2	785	36	60	198.3	0.033	1.50	3.94
F45	677,798	4,063,913	0.5	22.0	18.8	66	1030.9	53.6	574	21	54	216.1	0.031	1.23	4.21
F46	677,029	4,063,255	0.6	25.0	19.1	68	905.1	49.2	652	26	59	207.9	0.031	1.35	4.06
F48	675,028	4,060,955	0.8	26.1	19.7	69	712.9	40.3	830	36	56	182.2	0.033	1.41	3.63
F5	687,413	4,059,172	0.8	17.9	13.9	56	1083.9	65.8	593	42	66	257.3	0.059	1.14	4.81
F50	674,894	4,062,595	0.7	25.8	21.4	69	818.8	48.4	774	34	61	213.8	0.034	1.49	4.01
F51	675,922	4,063,775	0.6	28.5	21.8	74	915.7	51.7	642	31	60	214.8	0.034	1.43	4.20
F53	675,750	4,064,933	0.6	26.2	17.7	74	1035.0	57.1	566	20	58	220.3	0.039	1.34	4.19
F54	674,871	4,064,254	1.3	21.6	14.0	62	983.2	59.7	1013	15	46	289.5	0.039	1.43	4.01
F55	674,162	4,063,171	0.8	27.8	20.3	73	891.6	50.2	773	35	59	210.8	0.033	1.53	4.28
F59	673,793	4,064,755	<0.5	24.2	18.7	68	1039.7	53.9	601	22	55	221.6	0.032	1.32	4.20
F6	686,644	4,058,081	0.6	21.7	18.4	75	1161.2	61.6	584	30	60	264.3	0.049	1.39	4.90
F60	674,636	4,065,442	0.7	21.1	17.8	64	1147.8	56.9	629	32	52	256.6	0.033	1.21	4.51
F61	676,075	4,065,876	<0.5	21.0	8.5	48	1464.9	76.9	569	22	43	223.2	0.063	0.81	4.71
F62	674,501	4,066,666	<0.5	18.5	13.5	56	1279.8	62.2	550	18	43	235.4	0.027	0.97	4.25
F63	673,395	4,068,021	<0.5	15.6	11.9	49	1264.8	61.9	555	26	41	261.8	0.025	0.90	4.22
F64	672,902	4,068,383	<0.5	16.2	11.7	54	1029.8	55.0	566	29	47	382.1	0.031	1.10	4.07
F65	672,794	4,067,762	<0.5	18.2	12.8	57	1086.5	52.6	562	27	47	259.5	0.031	1.02	4.05
F66	672,606	4,067,052	<0.5	18.9	13.0	61	1054.1	53.5	494	20	48	256.3	0.032	1.22	4.11
F67	672,154	4,066,275	<0.5	19.5	15.0	59	1011.3	50.9	509	22	49	261.0	0.032	1.30	4.08
F69	671,900	4,065,635	<0.5	18.5	15.0	63	993.6	50.1	516	19	48	250.2	0.031	1.23	3.95
F7	686,293	4,060,059	0.6	20.2	15.3	57	962.2	53.2	515	36	57	242.3	0.043	1.14	4.31
F70	672,579	4,065,446	<0.5	18.0	15.0	57	1061.2	51.6	506	20	44	221.9	0.028	1.12	3.96
F71	673,064	4,065,097	<0.5	11.3	10.9	41	1029.5	47.7	402	25	34	148.9	0.018	0.64	3.36
F8	686,399	4,058,994	0.7	18.0	15.5	58	1012.6	55.0	526	36	64	248.4	0.047	1.25	4.52
F80	681,072	4,063,573	0.5	24.2	13.1	66	948.6	50.8	514	14	44	223.3	0.030	1.33	4.15
F81	680,053	4,064,611	0.6	17.2	13.0	63	1795.9	95.4	587	27	50	319.5	0.028	0.92	5.81
F82	677,457	4,064,661	<0.5	20.6	16.4	62	1222.5	58.2	576	22	48	236.1	0.031	1.10	4.43
F83	676,498	4,065,157	<0.5	20.6	12.0	53	1359.6	68.2	605	26	46	230.0	0.047	0.92	4.57
F84	674,888	4,066,139	<0.5	15.4	12.2	49	1316.0	65.7	544	19	42	225.7	0.033	0.85	4.25
F85	673,753	4,067,631	<0.5	14.2	12.4	47	1284.0	62.2	536	23	40	252.1	0.026	0.91	4.24
F9	685,095	4,058,061	0.7	19.4	17.2	57	1066.3	57.7	624	35	51	218.2	0.043	1.12	4.25
I-109	675,925	4,066,101	<0.5	24.1	9.5	49	1400.4	75.6	572	20	47	224.1	0.082	0.95	4.76
I-111	675,811	4,066,096	<0.5	27.9	10.5	59	1253.3	64.8	531	24	55	234.0	0.076	1.25	4.66
I-114	675,878	4,066,055	<0.5	22.0	10.3	52	1368.4	68.9	538	19	45	215.1	0.076	0.93	4.63
I-120	675,849	4,066,189	<0.5	21.6	8.5	51	1397.5	72.7	557	19	45	222.8	0.084	0.92	4.68
I-122	675,744	4,066,234	1.0	17.0	10.4	47	1357.2	65.4	494	17	38	248.5	0.062	0.79	4.25
I-129	676,008	4,066,072	0.5	23.8	9.9	55	1423.2	73.9	560	21	48	235.6	0.080	0.99	4.88
I-130	676,045	4,066,186	0.5	24.2	9.7	53	1437.7	73.3	564	22	48	234.0	0.081	0.94	4.85
I-131	675,971	4,066,261	<0.5	26.8	9.5	55	1398.1	76.0	577	20	50	237.5	0.092	1.04	4.91
I-132	675,906	4,066,352	<0.5	26.2	9.7	53	1361.6	75.2	573	18	50	234.4	0.104	1.07	4.87
I-135	675,938	4,066,008	<0.5	23.5	10.0	56	1407.9	73.6	572	22	48	226.9	0.080	0.98	4.81
Min			<0.5	11.30	8.50	41.00	712.90	40.30	402.00	13.00	34.00	148.90	0.02	0.64	3.36
Max			1.50	32.70	23.10	94.00	1795.90	99.40	1017.00	42.00	69.00	382.10	0.10	1.83	6.23
Mean			0.72	22.28	15.16	61.86	1093.53	59.53	587.91	25.12	52.13	235.72	0.04	1.22	4.37
Standard Deviation			0.20	4.42	3.70	10.04	242.64	12.31	116.17	7.09	7.76	39.70	0.02	0.24	0.56
Range			1.00	21.40	14.60	53.00	1083.00	59.10	615.00	29.00	35.00	233.20	0.09	1.19	2.87

$$C_f^i = \frac{C_i}{C_n} \quad (1)$$

According to Hakanson (1980) C_f^i <1 indicates low sediment contamination factor (cf); 1<C_f^i<3 indicates moderate cf.; 3<C_f^i<6 indicates considerable C_f^i>6 means very high cf.

3.4.2. Modified degree of contamination (mC_d)

Abrahim and Ghada (2005) modified the degree of contamination formula defined by Hotelling (1933) due to its limitations (because this formula was based on seven specified metals and an organic pollutant) and proposed a modified formula. This new formula is simply the sum of all contamination factors for a specified set of heavy metals divided by the number of analyzed heavy metals (n).

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (2)$$

Abrahim and Ghada (2005) proposed the following terminology to describe the modified degree of contamination: mC_d<1.5 none to very low degree of contamination (doc) (; 1.5≤ mC_d<2 means low doc; 2≤ mC_d<4 means moderate doc; 4≤ mC_d<8 means high doc; 8≤ mC_d<16 means very high doc; 16≤ mC_d<32 means extremely high doc; and means ultra-high doc.

3.4.3. Enrichment factor (EF)

Another method used to determine the pollution degree in the sediments due to anthropogenic factors is Enrichment Factor (EF). EF calculation is carried out by normalizing an element with respect to a reference element (Buat-Menard and Chesselet, 1979).

$$\mathrm{EF} = \frac{\left(\frac{C_n}{C_{ref}}\right)\text{sample}}{\left(\frac{B_n}{B_{ref}}\right)\text{background}} \quad (3)$$

where, C_n is the concentration of the examined metal in the sediment sample, C_{ref} is the concentration of the reference element in the sediment sample, B_n is the background value of the examined element, B_{ref} is the background value of the reference element such as Al or Fe. In this study, Fe is used as the normalizing element because its concentration is naturally high in the environment, and anthropogenic sources of contamination will have little effect on its concentration in a sediment sample. The terminology suggested by Sakan et al. (2009) was used to interpret EF values. Accordingly, EF < 1 indicates no enrichment; 1 < EF < 3 means minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; >50 is extremely severe enrichment.

3.4.4. Geo-accumulation index (Igeo)

Another commonly used quantitative approach to sediment contamination is defined by Müller (1969) and is called geo-accumulation index *(Igeo)*. This method assesses the degree of metal contamination by the following equation:

$$Igeo = log_2\left(\frac{C_n}{1.5B_n}\right) \quad (4)$$

In the above equation, C_n shows the concentration of the heavy metals determined in the sediment samples, and B_n is the background value of the element. Factor 1.5 was introduced as a correction factor and attributed to lithologic effects (Stoffers et al., 1986). Müller (1981) suggested seven classes of *Igeo*. These classes, *Igeo* values and the terminology are as follows: If *Igeo* values are ≤0, they belong to Class 0 (uncontaminated); if 0 < *Igeo* < 1 then they belong to Class 1 (uncontaminated to moderately contaminated); if 1 < *Igeo* < 2 then samples fall into Class 2 (moderately contaminated); if 2 < *Igeo* < 3 the samples will be in Class 3 (moderately to heavily contaminated); if 3 < *Igeo* < 4 then they will be in Class 4 (heavily contaminated); if 4 < *Igeo* < 5 the samples will be in Class 5 (heavily to extremely contaminated); samples having *Igeo* > 5 values will belong to Class 6, which would mean that these samples are extremely contaminated.

3.4.5. Pollution load index (PLI)

The Pollution Load Index, proposed by Tomlinson et al. (1980), is yet another tool used to evaluate heavy metal pollution. With this method, it is possible to determine the overall contamination status of a sample and examine how many times the metal content in the sediment exceeds the reference (pre-industrial) concentration. It is calculated using the below formula

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots\ldots \times CF_n)^{1/n} \quad (5)$$

where, CF is the contamination factor for each metal (or each site), and n is the number of contamination factors.

The *PLI* > 1 indicates pollution, whereas <1 indicates no pollution.

3.4.6. Potential ecologic risk factor (E_r^i)

The potential ecologic risk factor, which was developed by Hakanson (1980), is used to describe the impact of heavy metal contamination on organisms and ecosystems. The formula is presented as follows:

$$E_r^i = Tr^i \times C_f^i \quad (6)$$

where, Tr^i = Toxic response factor (These factors are defined by Hakanson (1980) as Zn = 1, Cr = 2, Cu = Pb = 5, As = 5) and C_f^i is the contamination factor described above.

The terminology proposed by Hakanson (1980) to describe the risk factor is as follows:

E_r^i<40 means low potential ecological risk (per); 40≤E_r^i<80 means moderate per, 80≤E_r^i<160 means considerable per; 160≤E_r^i<320 means high per and 320 means very high per.

3.4.7. Probability of toxicity (m-ERM-Q)

To evaluate the effect of heavy metal contamination of the sediments on the ecosystems and to understand the adverse biological effects, numerical Sediment Quality Guidelines (SQGs) can be applied. The SQGs provide effects-based, interpretive tools for sediment quality assessment. In this study, only the Effect Range Low (ERL) – Effect Range Median (ERM) guidelines proposed by Long et al. (1995) are used. ERL stands for the 10th percentile value and indicates concentrations below which adverse effects rarely occur. However, ERM stands for the 50th percentile value representing concentrations above which adverse effects occur frequently. The ERL-ERM guidelines can put forward the biological effect of a chemical mixture if the mean ERM quotient (m-ERM-Q) is calculated (Long et al., 1998). The formula of m-ERM-Q is presented as follows:

$$m-ERM-Q = \frac{\sum_{i=1}^{n} \frac{C_i}{ERM_i}}{n} \quad (7)$$

In the above formula, C_i is the concentration of the heavy metal under study in the sample, ERM is the Effect Range Median explained in the above text and n is the total number of studied elements.

Long et al. (2000) related m-ERM-Q to the probability of toxicity as follows: An m-ERM-Q < 0.1 has 9 % probability of toxicity, whereas 0.11 < m-ERM-Q < 0.5 has 21 % probability of being toxic. However, 0.51 < m-ERM-Q < 1.5 has 49 % probability of toxicity and m-ERM-Q > 1.5 has about 76 % probability of being toxic.

4. Results and discussion

4.1. Spatial distribution of the studied elements

The mean concentrations of 13 elements analyzed in 69 sediment samples collected from Fethiye-Göcek Bay follow the order: Fe > Al >

Ni > Mn > Ti > Cr > Zn > Co > V > As>Cu > Pb > Mo (Table 1). If these mean concentrations are compared to the typical Earth crust's values (Turekian and Wedepohl, 1961) it can be seen that the mean As (25.2 ppm), Cr (235.72 ppm), Ni (1093.53 ppm) and Co (59.53 ppm) concentrations are higher than those values reported for Earth's crust (Table 2; Fig. 2).

The spatial patterns of the elements under consideration in this study are presented in Fig. 3. According to Fig. 3a, the minimum Aluminum (Al) concentrations are observed around the coastline close to Göcek, and the area where the İnlice stream enters the Mediterranean Sea. The concentrations gradually increased upon moving away from the coast. The highest concentrations are observed at two locations, F-1 and F-18, which are about 0.6 % higher than the mean Al concentrations. It is worth mentioning that, around sampling point F-1 Fethiye harbor is located and human sources of element input are possible around the harbor area (not only for Al but also for other elements as well). The anthropogenic sources of element input to the harbor area include a) discharge of the Murtbeli River carrying agricultural drainage waters and the treated wastewater of Fethiye Town, b) wastewater generated by the boats at Fethiye Marina and c) domestic waste of settlements and tourism facilities which are not connected to the municipal wastewater collection system (Yildirim and Balas, 2019; Yılmaz et al., 2017).

Fig. 3b represents the Arsenic (As) concentrations in the sediment samples. In this figure, the lowest concentrations, which are close to Earth crust's values are located in between Fethiye and Göcek cities, just at the area where the İnlice and Çayboğazı River flows into the Mediterranean Sea. This freshwater input and the sediments transported with this stream have affected the sediment chemistry. When the higher concentrations are considered, an increase in the As concentrations can be observed around the Fethiye and Göcek harbors in addition to the area around sample F-42, located away from the coast. This finding is discussed in Section 4.4.

In Fig. 3c, Co concentration distribution map is presented. Unlike Al, the lowest Co concentrations are observed both away from the coast and in the area where the Çayboğazı River meets the sea. In contrast, the highest concentrations are observed near the Fethiye harbor and at sampling point F-81. There is also a slight increase toward Göcek harbor. It should also be mentioned that near the subaqueous hot spring (SUB-7) there is also an increase in the Co concentrations. As briefly mentioned earlier, Avşar et al. (2017) implemented horizontal temperature measurements in Fethiye-Göcek Bay and detected a subaqueous hot spring (SUB-7). Avşar et al. (2017) also carried out ITRAX μXRF scanning studies and obtained semi-quantitative distributions of 19 elements (As, Br, Ca, Cl, Cr, Fe, K, Mn, Ni, Pb, Rb, Se, Sr, Si, S, Ti, Y, Zn, Zr) in Fethiye Göcek Bay (Avşar et al., 2017). Their results revealed out that the subaqueous hot springs are enriched in some elements and Co can be another element affected from the occurrence of this subaqueous hot spring and the hydrothermal activity associated with this spring.

Fig. 3d shows the spatial distribution map of Cr. The highest Cr concentrations are observed in both Fethiye and Göcek harbors. Around

Table 2
Sediment assessment method results for Fethiye-Göcek Bay for the studied elements (the concentrations are in ppm except for Al, Fe and Ti, which are in %).

Element concentration	As	Cr	Cu	Ni	Pb	Zn	Co	Mn	Mo	V	Al (%)	Fe (%)	Ti (%)
Mean	25.12	235.72	22.28	1093.53	15.16	61.86	59.53	587.91	0.72	52.13	1.22	4.37	0.04
Min	13	148.9	11.3	712.9	8.5	41	40.3	402	<0.5	34	0.64	3.36	0.02
Max	42	382.1	32.7	1795.9	23.1	94	99.4	1017	1.5	69	1.83	6.23	0.1
STD	7.09	39.7	4.42	242.64	3.7	10.04	12.31	116.17	0.2	7.76	0.24	0.56	0.02
Earth crust's values*	13	90	45	68	20	95	19	850	2.6	130	8	4.72	0.46
Toxic Response** Factor	10	2	5	n.a.	5	n.a.	1	n.a.	n.a.	n.a.	n.a	n.a.	n.a.
ERM***	70	370	270	51.6	218	410	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	n.a.
ERL***	8.2	81	34	20.9	46.7	150	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	n.a.
Contamination factor													
Mean	1.93	2.62	0.50	16.08	0.76	0.65	3.13	0.69	0.28	0.40	0.15	0.93	0.09
Min	1.00	1.65	0.25	10.48	1.70	0.43	2.12	0.47	0.00	0.26	0.08	0.71	0.04
Max	3.23	4.25	0.73	26.41	0.11	0.99	5.23	1.20	0.58	0.53	0.23	1.32	0.22
STD	0.55	0.44	0.10	3.57	0.08	0.11	0.65	0.14	0.08	0.06	0.03	0.12	0.04
Enrichment factor													
Mean	2.08	2.82	0.53	17.29	0.82	0.70	3.37	0.74	0.30	0.43	0.16	1.00	0.09
Min	1.08	1.78	0.27	11.27	1.83	0.46	2.28	0.51	0.00	0.28	0.09	0.77	0.05
Max	3.47	4.57	0.78	28.40	0.11	1.06	5.63	1.29	0.62	0.57	0.25	1.42	0.23
STD	0.59	0.47	0.11	3.84	0.09	0.11	0.70	0.15	0.08	0.06	0.03	0.13	0.05
Geoaccumulation Index													
Mean	0.37	0.80	−1.60	3.42	−0.98	−1.20	1.06	−1.12	−2.44	−1.90	−3.30	−0.70	−4.11
Min	−0.58	0.14	−2.58	2.81	−1.82	−1.80	0.50	−1.67	−8.61	−2.52	−4.23	−1.08	−5.11
Max	1.11	1.50	−1.05	4.14	−0.38	−0.60	1.80	−0.33	−1.38	−1.50	−2.71	−0.18	−2.79
STD	−1.46	−1.77	−3.93	1.25	−3.02	−3.83	−1.21	−3.46	−4.29	−4.65	−5.64	−3.66	−5.11
Potential ecological risk factor													
Mean	19.32	5.24	2.48	n.a.	3.79	n.a.	3.13	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Min	10.00	3.31	1.26	n.a.	8.50	n.a.	2.12	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Max	32.31	8.49	3.63	n.a.	0.53	n.a.	5.23	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
STD	5.45	0.88	0.49	n.a.	0.40	n.a.	0.65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Modified degree of contamination					Pollution load index				Mean ERM quotient			
Mean	2.17					0.80				3.46			
Min	1.48					0.28				2.23			
Max	3.46					1.10				5.64			
STD	0.46					0.16				0.73			

* Earth crust's values are taken from Turekian and Wedepohl (1961)
** Toxic response factors defined by Hakanson (1980)
*** ERL and ERM guidelines are taken from Long et al. (1995) See text for further explanation

n.a. not available.

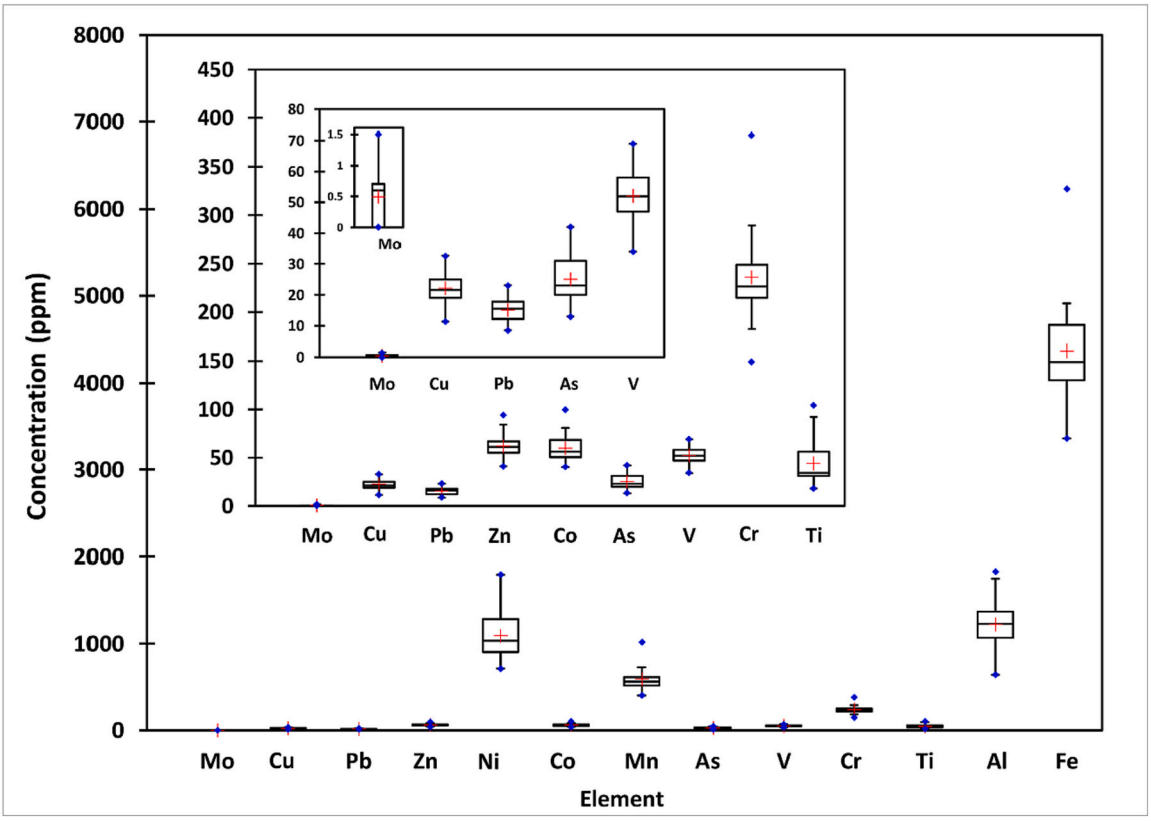


Fig. 2. Box plots of trace metal concentrations in the coastal sediment samples of Fethiye-Göcek Bay.

sample F-81 and SUB-7, there is an increase in the concentrations. These elevated concentrations, up to 380 ppm, gradually decrease away from the coast. The lowest Cr concentrations near the coastal area are located where the Çayboğazı stream meets the Mediterranean Sea.

The spatial distribution of Cu is highly interesting because the lowest Cu concentrations can be observed near the Göcek harbor, whereas the highest values are around the SE part of the Fethiye harbor (Fig. 3e). The sampling points located around the northern part of Fethiye harbor also exhibited low levels of Cu. This area is where the Susambeli stream flows into the sea. There is a gradual increase in the Cu concentrations moving away from the coast. Likewise Co, Cu is also high around SUB-7.

Fe distribution map is presented in Fig. 3f. In this map, the highest Fe concentrations are observed around the Fethiye harbor area and F-81. There is also an increase around SUB-7. The concentrations are relatively low around Göcek harbor and away from the coast. Again, the area where the Çayboğazı River enters the sea, the lowest Fe concentrations can be seen, following the same pattern as As and Co.

In Fig. 3g, Mn distribution map is given. This map suggests that the highest Mn concentrations are observed in relatively offshore samples (F-42 and F-54). There are also elevated concentrations observed around Fethiye harbor (F-1, F-2, F-3 and F-4). The lowest concentrations are located around the areas where the Çayboğazı and İnlice River's flow into the sea.

Fig. 3h shows the Mo element distribution map. According to this map, the lowest Mo concentrations can be found around the Göcek harbor, whereas the highest concentrations can be observed around sampling points F-12, F-54 and F-42.

The spatial distribution of Ni concentrations in the sediment samples is presented in Fig. 3i. There seems to be an anomaly in sample F-81 where the highest Ni value can be observed (Fig. 3i). Besides, the lowest Ni values are observed away from the coast and where the Çayboğazı River meets the sea, whereas there is an increase in the concentrations in locations where the Fethiye harbor and SUB-7 is located.

Regarding Pb concentrations (Fig. 3j), the lowest values are around the coastal line, except for the sampling points near Fethiye harbor (F-1 has the highest Pb). Samples collected away from the coast also had high Pb concentrations (F-23, F-33, F-50 and F-51). Fig. 3k shows the Ti distribution map. According to this map, the highest Ti value was recorded around SUB-7. High concentrations can also be observed around Fethiye harbor.

In Fig. 3l, V concentration distribution map is presented. According to this map, the highest V concentrations are located around the Fethiye harbor. However, the lowest concentrations can be observed around the Göcek harbor and the areas where the İnlice and Çayboğazı Rivers flow into the sea. Relatively higher concentrations are also observed offshore in two samples (F-44 and F-50). Lastly, Fig. 3m shows the concentration distribution map of Zn. Likewise V, the highest concentrations of Zn are observed around the Fethiye harbor whereas the lowest ones are around the Göcek harbor and the area where the İnlice and Çayboğazı Rivers flow into the sea. This freshwater input to the sea influences sediment chemistry, decreasing the concentrations of certain elements like Zn, As, Co, Cr, Fe, Mn, Ni, Pb and V. As mentioned earlier, at the present, some of these rivers have low discharge rates (Koç, 2012). However, they might have affected the sediment geochemistry in the past when they have considerably high discharges, i.e., when they had the power of shape the morphology of the area and bringing sediments having relatively lower concentrations of the aforementioned elements. Milliman and Syvitski (1992) stated that past fluxes of river sediment discharge to the sea is impossible to calculate; however, the ancient fluxes are different from today's.

Besides, it should also be noted that elemental concentrations in marine sediments are also affected by reactions at particle surfaces (like adsorption/desorption and reduction/oxidation reactions) with the physical transport, dilution and sorting of sediments (Luoma, 1990). Luoma (1990) also stated that natural depositional processes influence the final distribution of the metal load associated with the particulate

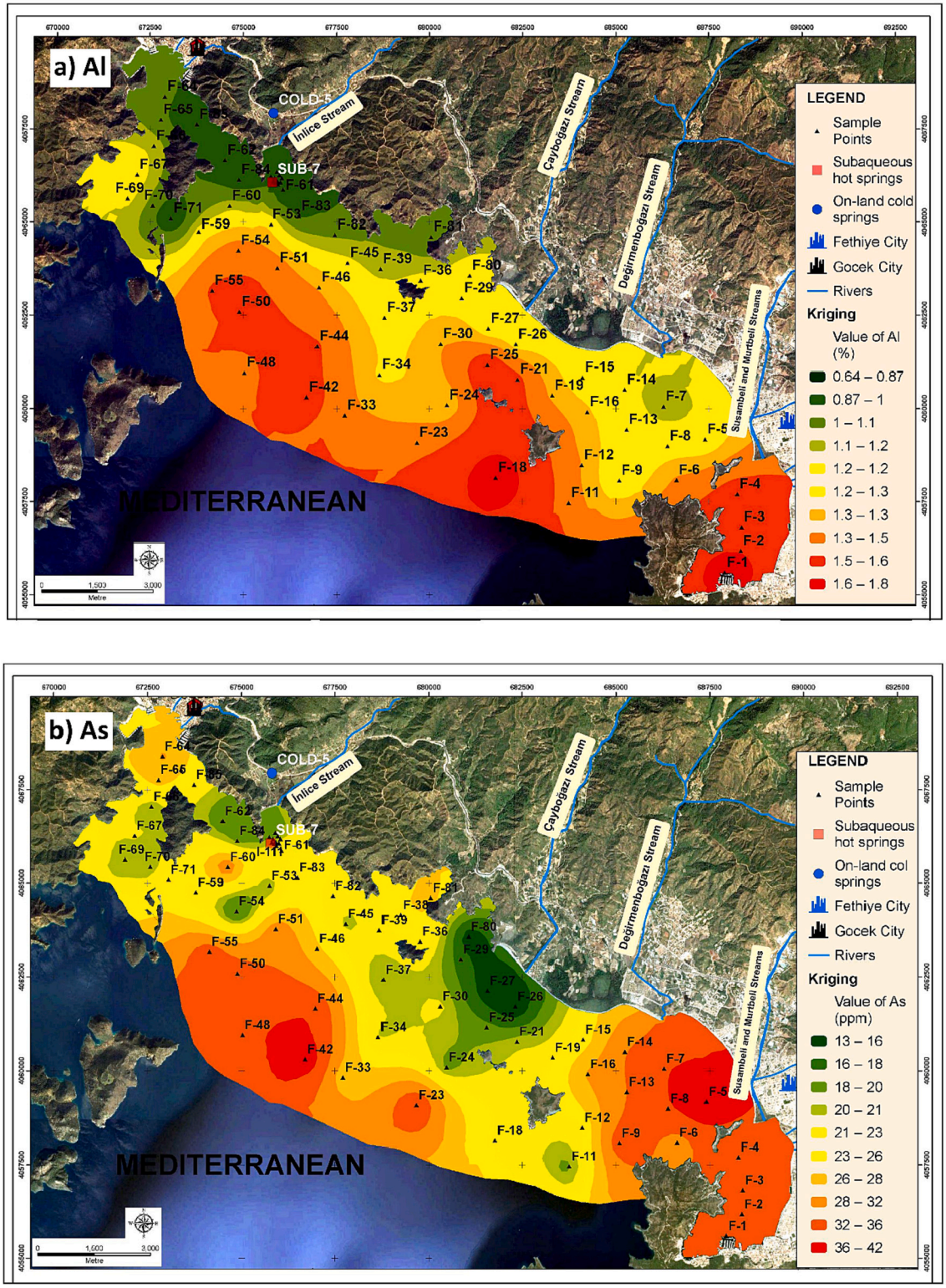


Fig. 3. Spatial distribution of the studied elements of the Fethiye-Göcek Bay: a) Al, b) As, c) Co, d) Cr, e) Cu, f) Fe, g) Mn, h) Mo, i) Ni, j) Pb k) Ti, l) V, m) Zn.

material. In any case, as stated before, the anthropogenic input of some trace metals is prominent in especially around Fethiye harbor since the concentrations show a decrease away from the harbor area. The decline in trace metal concentrations away from the source of anthropogenic inputs is attributed to the extent of dilution with less contaminated sediments and both the water and particulate movement (Luoma, 1990).

4.2. Correlation, cluster and principal component analysis results

Table 3 displays the Pearson correlation coefficient matrix for the studied elements. Overall, Pb—Zn, Cu—Zn, Ni—Co, Fe—Ni, Fe—Cr, Fe—Co, Al—Cu, Al—Pb, Al—Zn, Pb—V, and Al—V yielded high positive correlations ($R > 0.70$, Table 3). The dendrogram obtained from the R-

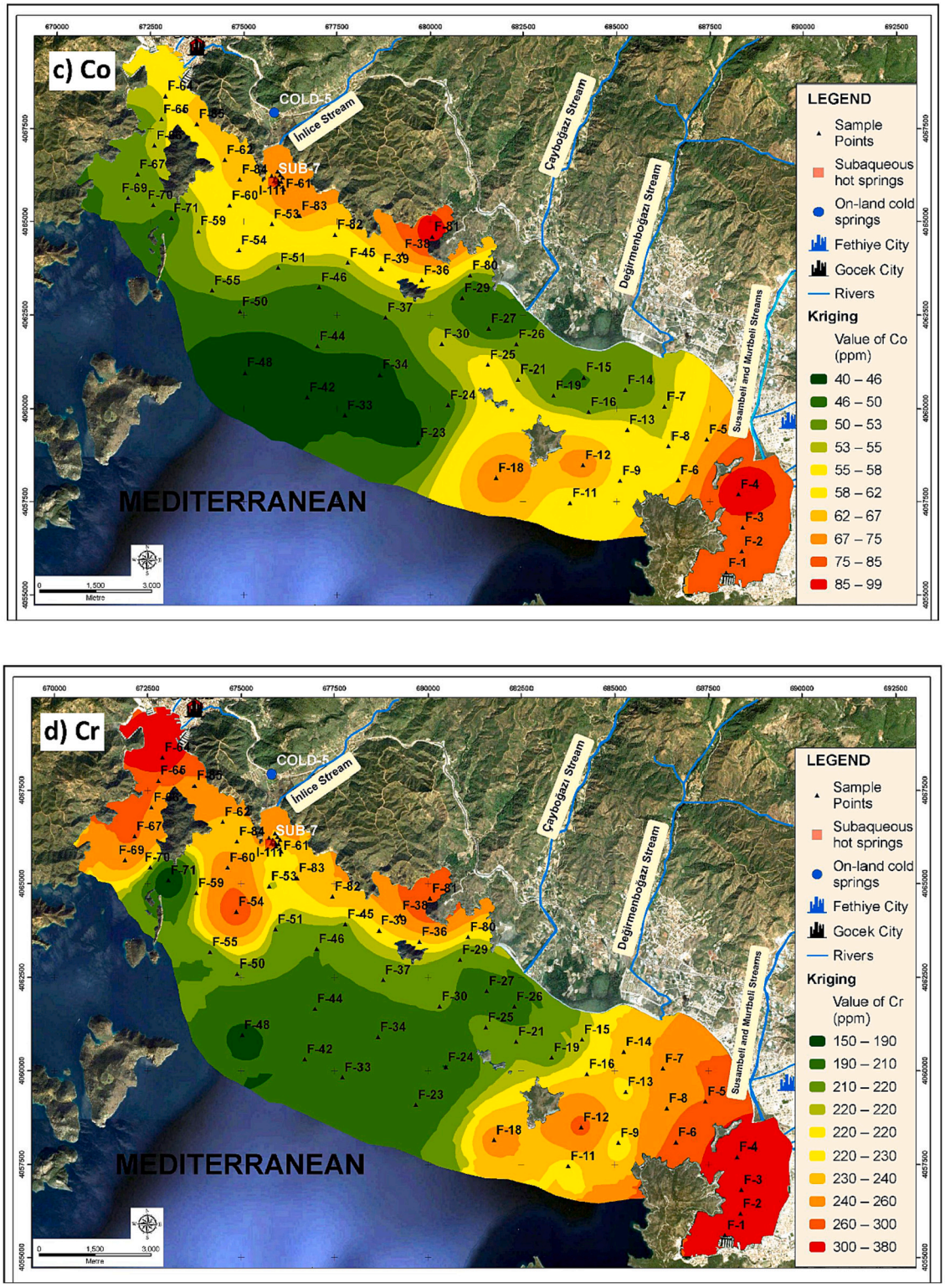
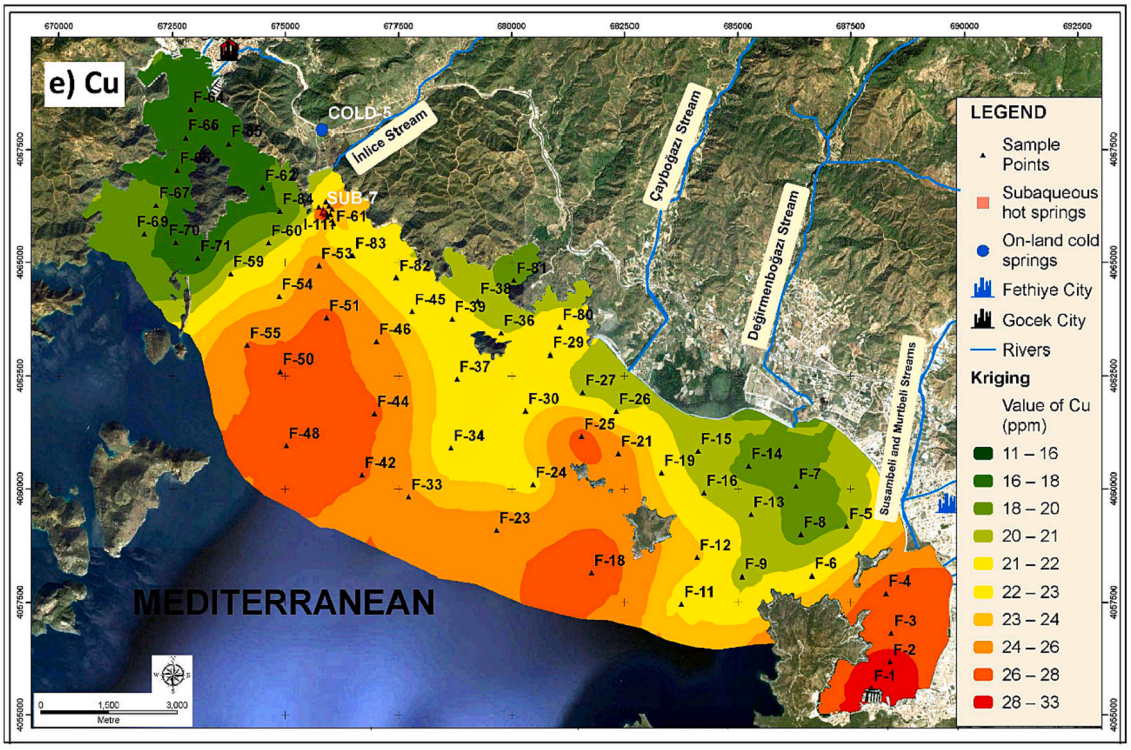


Fig. 3. (*continued*).

mode HCA analysis of the elements is consistent with the Pearson correlation analyses (Fig. 4). According to Fig. 4, two clusters are obvious. Cluster 1 includes Co, Ni, Fe, Cr and Ti and Co- Ni pair has got the highest similarity, and they are highly similar to Fe. This explains the high correlation coefficients between Co- Ni- Fe. Cluster 2 includes elements Al, Zn, Pb, V, Cu, Mo, As and Mn. This cluster suggests that the highest similarity is between Al and Zn. Al—Zn is also highly similar to Pb, and then to V. This is also the reason why the Pearson correlation matrix suggests a high correlation between Al- Zn, Al—Pb, Pb—Zn, Pb-Vn and Al—V.

Cluster 1 elements most probably represent the lithogenic influence of the geological units around the study area. Fe, Cr and Ti form insoluble hydroxides and immediately after they enter the oceans as suspended soils and prevail as solid phases (they have short residence times in sea water) (Goldberg and Arrhenius, 1958). Besides, Cr and Ni are the well-known products of the chemical weathering of mafic/ultramafic



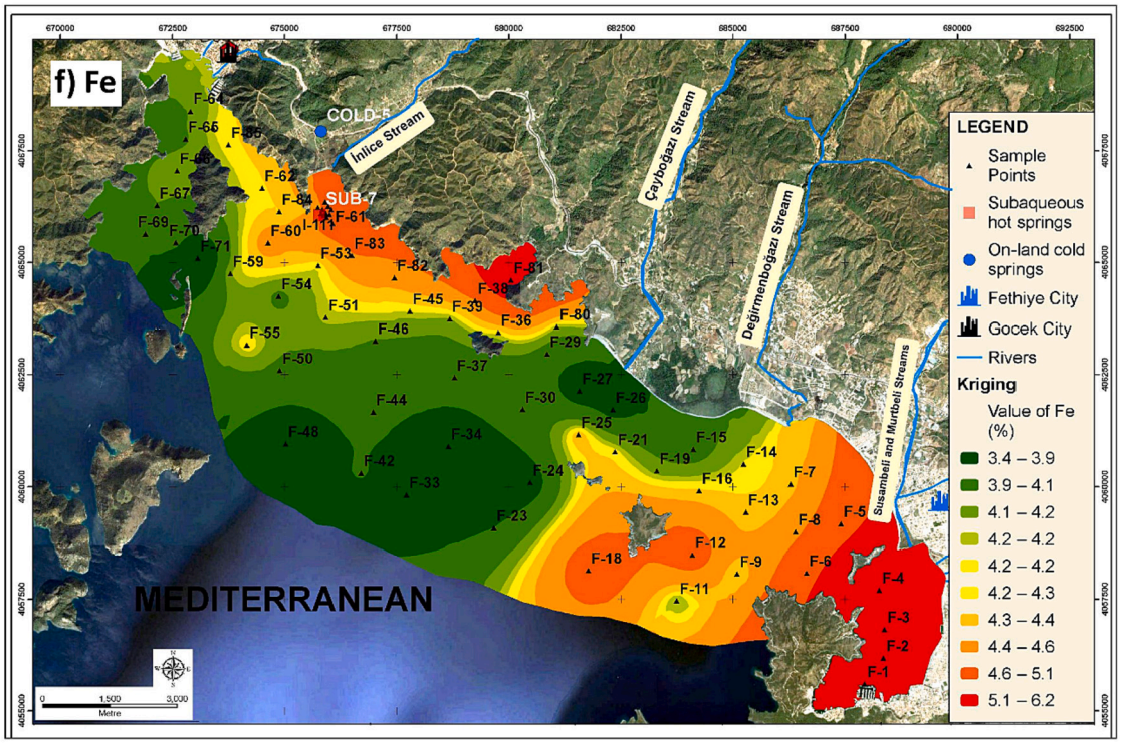


Fig. 3. (*continued*).

rocks [55 and many others] and the prevalently outcropping geological unit in the study area is peridotite. Ni and Co are highly correlated hence they should have a common source and mutual dependence. Therefore, the source of the elements in Cluster 1 is most probably the weathering of the geologic units, especially the peridotites. The enrichment of the metals Cr, Ni and Co relative to Earth crust's values can also be attributed to the natural chemical weathering of peridotites. The cluster 2 elements include Al, Zn, Pb, V, Cu, Mo, As and Mn. There is a high correlation between Al, Zn, P and V, probably indicating a common source. In this cluster of elements, anthropogenic influence might be responsible for enrichment in the concentrations around the near shore areas of the bay and only arsenic is enriched relative to the Earth crust's values. There is an enrichment of some of the Cluster 2 elements (Cu, Pb, Zn and As) around sample F42. In this area, as will be explained in the following section, there might be a hydrothermal activity affecting the sediment chemistry. According to the HCA, the geochemical behavior of

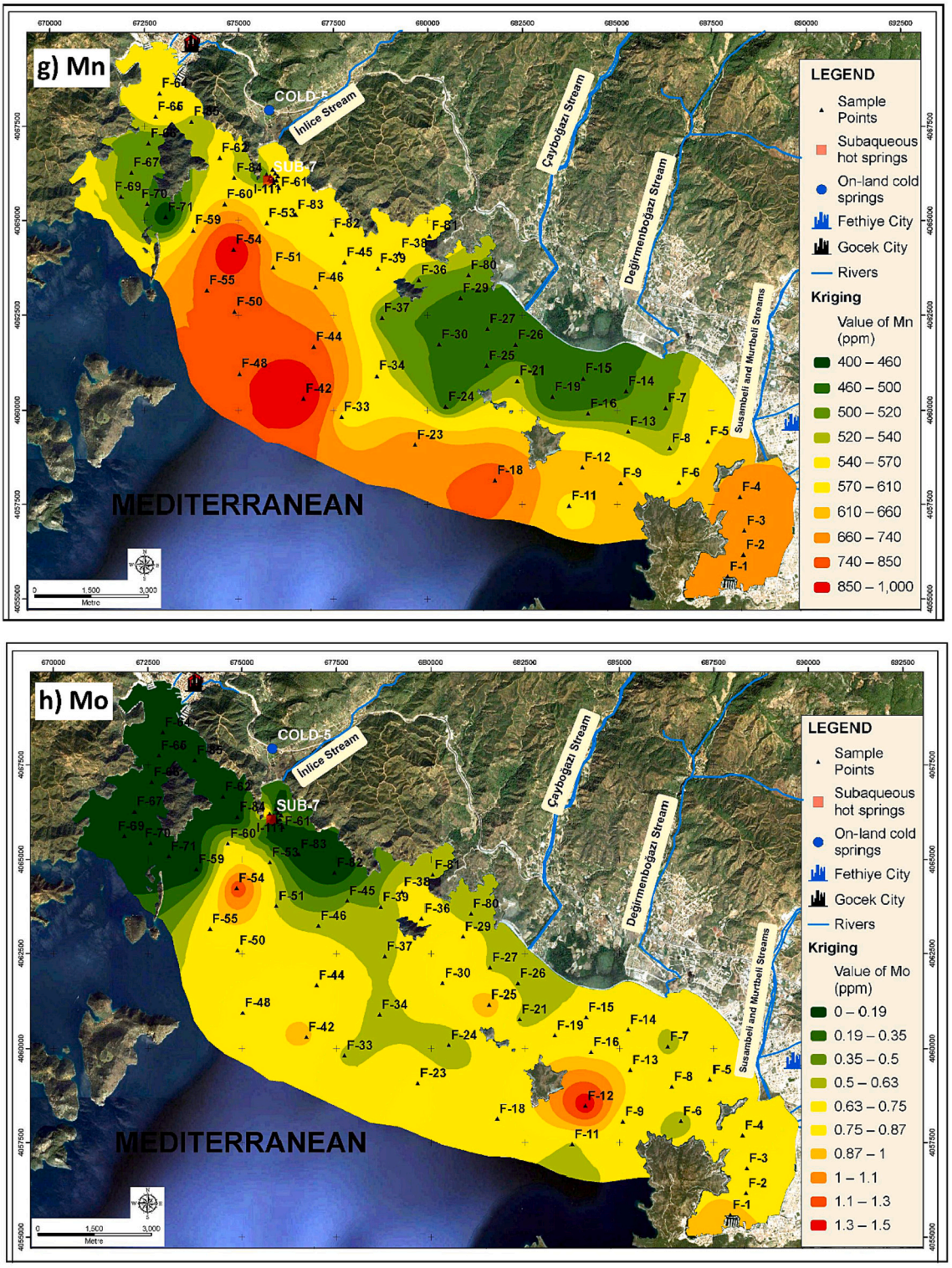


Fig. 3. (*continued*).

As and Mn seems to be different from that of the other metals. The strong correlation between As and Mn can be explained by the presence of As adsorbed onto Manganese (Mn) oxides. Mn oxides have adsorptive capabilities and can oxidize reduced species like As (III) (Beinlich et al., 2018).

According to the PCA, the first two axes of the analysis explained almost 70 % of the data variation, the first axis being responsible for almost 40 % of this variation (Fig. 5). Fig. 5 shows that Axis I is positively correlated with the elements Mo, Cu, Pb, Zn, Co, Mn, As, V, Cr, Al and Fe; negatively correlated with Ni and Ti. However, Axis II is positively correlated with Cu, Zn, Ni, Co, Mn, As, V, Cr, Ti and Fe; negatively correlated with Mo, Pb, and Al. Since As and Fe shows correlation in different axes, it can be stated that As is not bound to Fe-oxides in the study area (in fact, as stated earlier, As is more probably bound to Mn-oxides). The dominant elements in PC2 were Ni, Co, Cr, T, and Fe. This principal component represents the lithological effects on

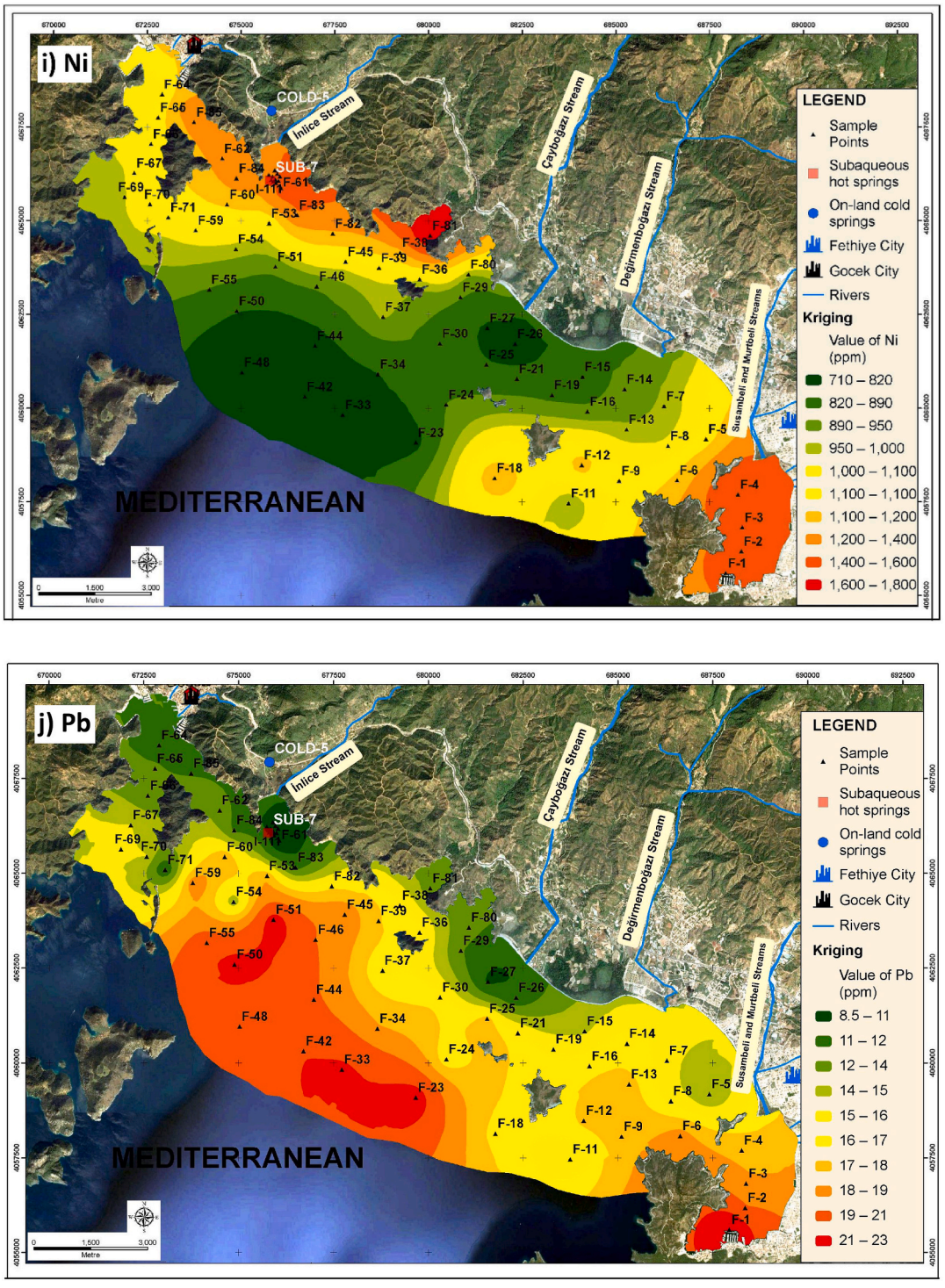


Fig. 3. (*continued*).

the sediment geochemistry. In contrast, PC1 includes Mo, Cu, Pb, Zn, Mn, As, V, Al and Fe. This component is about the anthropogenic effects and the impact of possible hydrothermal activities.

4.3. Contamination evaluation

After the application of certain contamination analysis methods such as contamination factor, modified contamination degree, pollution load index, m-ERM-Q and the probability of toxicity some interesting results were obtained in this study. Accordingly, the element with the maximum contamination factor value was Ni (C_f^{Ni} >6 for sample F-81). This indicates a very high sediment contamination with respect to Ni. However, the maximum contamination factors for Co, Cr and As are between 3<C_f^{Co}, C_f^{Cr}, C_f^{As} <6 suggesting considerable contamination. Except for Fe and Mn, the remaining elements showed low sediment contamination factors. For Fe and Mn, the contamination factors were moderate. If the mean contamination factors are considered Fe and Mn, then these two elements also indicate low $C_f^{Fe,\ Mn}$.

The Enrichment Factor (EF) values are almost similar to the contamination factor values: Ni has got the highest EF (belonging to

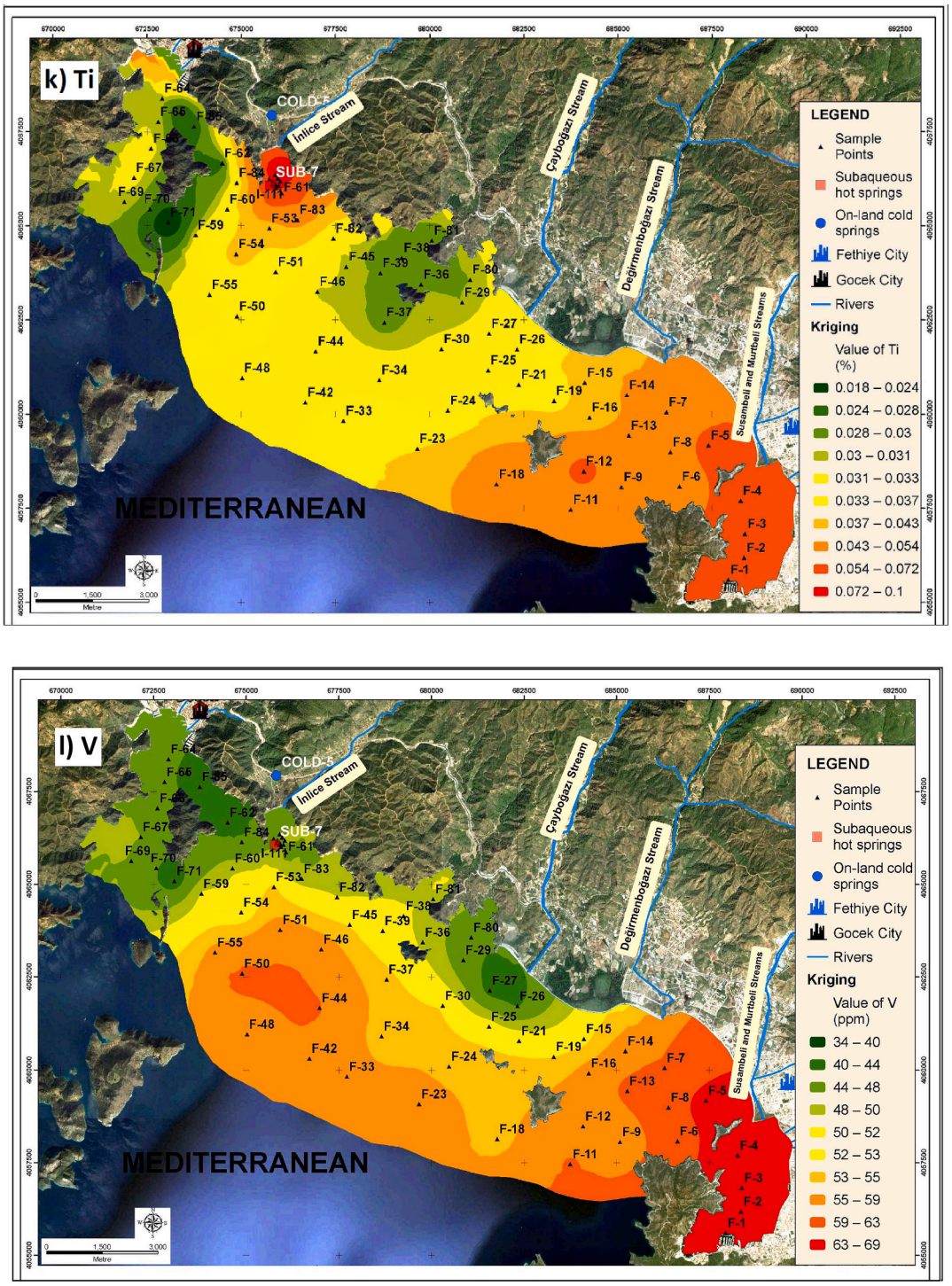


Fig. 3. (*continued*).

sample F-81), followed by Co (sample F-81), Cr (sample F-64), As (sample F-42).

The Geoaccumulation Index calculations show that none of the samples are extremely contaminated with respect to the studied elements. However, according to the maximum Igeo values, Igeo of Ni falls into Class 5 for sample F-81, which means this sample is heavily to extremely contaminated with respect to Ni. For the rest of the elements, unsurprisingly, Co (F-4), Cr (F-64) and As (F-5) fall into Class 2, suggesting that these samples are moderately contaminated with respect to the mentioned elements.

The potential ecological risk factors calculated for As, Cr, Cu, Pb and Co indicate low ecological risk with respect to these elements since the factor values are lower than 40 for all elements.

The modified degree of contamination calculations yielded the following results: The mean-modified degree of contamination is 2.17 (maximum is 3.46), this value indicates that there is a moderate degree of overall contamination in the study area. However, pollution load index, giving the overall contamination status of a sampling site, indicates that there is no pollution (PLI < 1) when the mean concentrations are considered. However, if the maximum concentrations are used in the calculations, then there is a pollution (PLI > 1). Finally, mean ERM quotient calculations based on As, Cr, Cu, Ni, Pb, and Zn

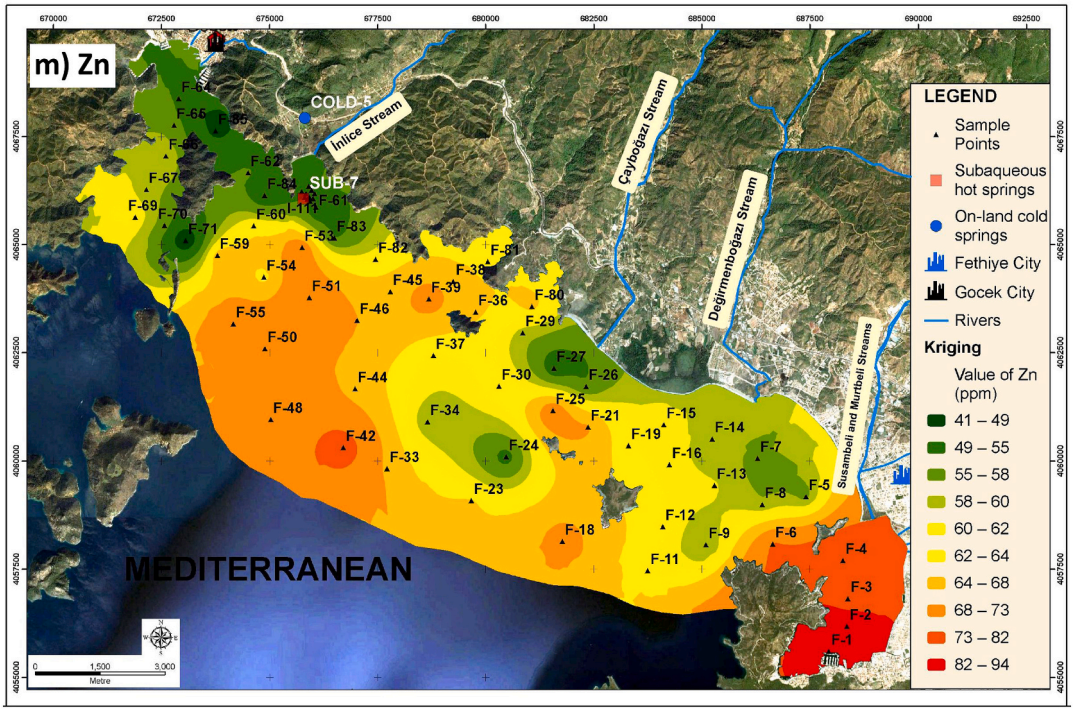


Fig. 3. (*continued*).

Table 3
Pearson's correlation coefficients between the studied elements.

	Mo	Cu	Pb	Zn	Ni	Co	Mn	As	V	Cr	Ti	Al	Fe
Mo	1												
Cu	0.367**	1											
Pb	0.552**	0.457**	1										
Zn	0.501**	**0.745****	**0.776****	1									
Ni	−0.347**	0.019	−0.469**	−0.100	1								
Co	−0.0974	0.238*	−0.341**	0.091	**0.927****	1							
Mn	0.389**	0.507**	0.472**	0.509**	−0.034	0.093	1						
As	0.332**	0.223	0.576**	0.419**	−0.09	−0.013	0.457**	1					
V	0.523**	0.600**	**0.720****	**0.735****	−0.151	0.051	0.405**	0.685**	1				
Cr	0.044	0.093	−0.022	0.317**	0.564**	0.623**	0.181	0.203	0.229	1			
Ti	−0.135	0.347**	−0.441**	−0.119	0.586**	0.633**	0.056	−0.045	0.090	0.187	1		
Al	0.602**	**0.745****	**0.751****	**0.848****	−0.401**	−0.141	0.512**	0.343**	**0.725****	0.141	−0.156	1	
Fe	0.067	0.423**	−0.054	0.390**	**0.806****	**0.910****	0.180	0.243*	0.371**	**0.704****	0.575**	0.139	1

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

concentrations give the probability of toxicity as 76 % which is the highest level of probability. This result was obtained even if the minimum concentrations of these TMs are used in the calculations.

4.4. Focusing on the enriched elements: As, co, Cr and Ni

The spatial and correlation analyses, HCA, PCA and contamination evaluation methods together indicate that some TMs are threatening the ecology and living organisms in the study area. Hence, As, Co, Cr and Ni metals are the ones that should be focused on. Arsenic (As) is a naturally occurring metalloid known to be toxic for humans (inorganic arsenic is a human carcinogen), and other living organisms (Manning et al., 1994). It is used in herbicides and insecticides, and as a wood preservative in addition to its usage in electronics, medicine, and industry (Nriagu and Azcue, 1990). In the environment, As and its compounds are highly mobile, and they cannot be extinguished (Chung et al., 2014). Chronic exposure to arsenic-contaminated water, food, or air can have harmful health effects on humans (WHO, 2001; Argos et al., 2010). Cr is a metal essential for human metabolism to organize the insulin movement in the body and the estimated safe and adequate daily dietary intake of Cr is reported as 250 μg Cr per day (National Research Council, 1989). The possible sources of Cr are the combustion of fossil fuels, wood and paper and industrial oxidation of the Cr-bearing minerals (Kahvecioglu et al., 2003). Ni is a metal mostly used in Ni—Cd batteries, coins, stainless steel and electroplating (Pandey and Singh, 2017). The possible pollution sources of Ni are forest fires, volcanic activities, coal smoke, diesel and fuel oils, waste of mining activities and Ni—Cd batteries (Yahaya, 2011; Martinez-Ruiz and Martinez-Jeronimo, 2015). Ni is an essential metal for humans but its high concentrations can have toxic effects (Bielmyer et al., 2013) like stomach and lung cancer according to a study on the nickel refinery workers in Russia, England and Japan (Vural, 1993). Co is another essential metal that is a part of vitamin B-12 and is essential for maintaining the nervous system and red making blood cells Human daily dietary intake of cobalt changes between 5 and 50 μg. Co is mostly used in the steel industry, to manufacture hard metals and alloys (Lison, 2007). It usually occurs with other metals such as Ni, Cu, Mn and As. Volcanic eruptions, soil, dust, seawater, forest fires, burning coal and oil, vehicle exhausts and industrial processes are the natural and

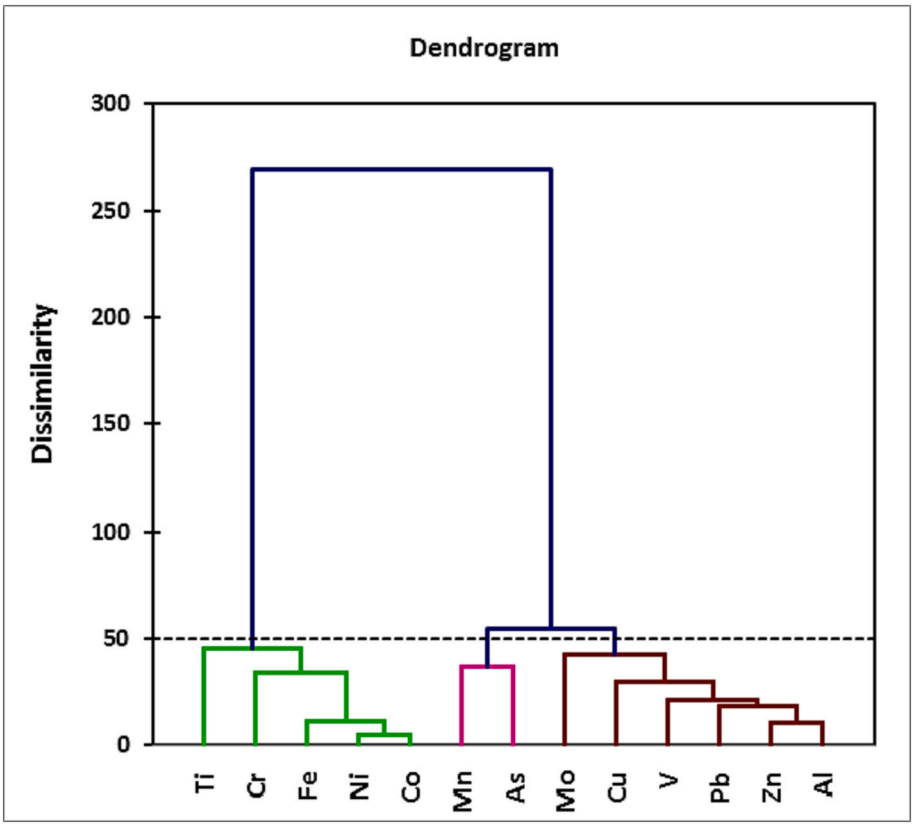


Fig. 4. Dendrogram obtained by R-mode HCA of the chemical constituents in sediment samples.

anthropogenic sources of cobalt in the environment (Ministry of Environment (Ontario Canada), 2011).

Hellmann (1970) made a classification of trace metals in recent sedimentary deposits as lithogenic (geochemical) and anthropogenic (man-made or civilizational). This classification was based on the predominant source of the trace metals. Accordingly, the second group included Pb, Cu, Zn as well as Co, Ni, Cr, and many others. In the study area, there is also a civilizational component to these elements, namely Co, Cr, and Ni, since all three elements show enrichment by a factor of 2 with respect to the minimum recorded concentrations near both Fethiye and Göcek harbors. However, the minimum concentrations are nearly 3 times enriched relative to the Earth Crust's values (Turekian and Wedepohl, 1961) for Co and Cr, and this enrichment is 16 fold for Ni. This anthropogenic component is masked by the lithogenic component since the statistical results that we obtained here are coherent with the geology of the area. Of course, the high concentrations of Ni, Co and Cr around the harbor areas can be attributed to anthropogenic sources such as the population, coal smoke (coal is used in the area during winter for heating purposes) and diesel and fuel oils used by the cars, boats or ships visiting these crowded harbors.

Arsenic is another pollutant that deserves a focus in this paper. This trace metal, highly toxic to humans as mentioned earlier, is enriched especially near Fethiye harbor and to some extent near the Göcek harbor. These enrichments can be attributed to anthropogenic sources like petroleum products used in ships or the arsenical pesticides used in agriculture and transported along the Susambeli and Murtbeli Streams near Fethiye harbor. The enrichment of arsenic near samples F-42, F-48, F-44, F-50 and F-55 should be natural (Fig. 3b). Together with As concentrations (Fig. 3b), other elements like Cu (Fig. 3e), Pb (Fig. 3j) and Zn (Fig. 3k) also exhibit elevated concentrations. HCA analyses revealed out that these elements are interrelated and this finding can well be an indication of the presence of a submarine hydrothermal vent in this area because these elements are defined as chalcophile hydrothermal precipitates (Megalovasilis and Godelitsas, 2015). Submarine hydrothermal venting activities have been reported in previous research studying subaqueous hot spring occurrences in Fethiye-Göcek Bay (Avşar et al., 2017) and hydrothermal influence on near shore sediments in the islands of Greece (Voudouris et al., 2021; Acosta et al., 2013). Acosta et al. (2013) also stated that shallow-water hydrothermal systems could have chemical impacts on immediate environments. However, further investigations are necessary to reveal the exact mechanisms of the As enrichment.

5. Conclusions

A complex order of processes can affect the trace metal concentrations in aquatic systems. Urbanization, industrialization and rapid growth of population are only some factors that can cause various contaminants to enter a surface water system and these contaminants are transported to the bay areas with rivers. Usually, only a small part of these contaminants stays dissolved in the seawater after reaching the bay area, they got deposited inside the surface sediments. In some cases, when the physical and chemical conditions change, these contaminants can re-enter the water body posing considerable threat to the ecosystem of the area. Therefore, investigation of the trace metal contamination status of the sediments in such aquatic systems is critical. In fact, the trace metal contamination in the aquatic systems has received considerable attention recently due to the toxicity, persistence, abundance and bio-accumulation of most of the trace metals. In this study, the trace metal contamination levels, the possible sources of contamination and the effects of the trace metals on the ecosystem of the Fethiye-Göcek Bay are investigated using the data obtained from the sea bottom sediment samples collected from 69 different points. According to the results of this study, the zones that were utmost affected by trace metal contamination are located around the Fethiye and Göcek harbors, around SUB-7 subaqueous hot spring, and sampling location F-81. The Fethiye harbor

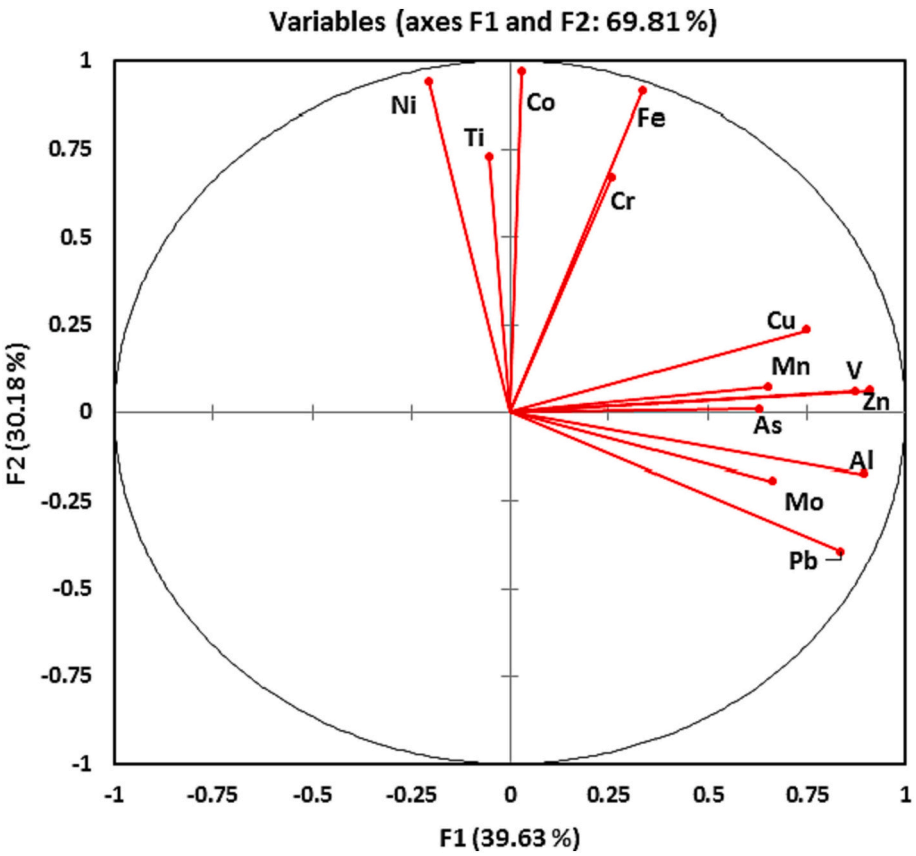


Fig. 5. Ordination diagram for the first two components of the PCA results. PCA was carried out by considering all of the studied elements. The analysis explained 69.81 % of the data variation and the first axis is responsible for almost 40 %.

and F-81 sampling point have the highest contamination factor (very high level) and modified contamination degree (moderate level). The maximum contamination factors calculated for As, Co, Cr and Ni indicate considerable contamination. Ni made the highest contribution toward the Pollution Load Index of the study area since the minimum recorded Ni concentrations are enriched almost 9 times relative to Earth Crust's values. Ni had a strong correlation with Co. The sources of these trace metals are both anthropogenic and natural. Additionally, mean ERM quotient values revealed out that the probability of toxicity is 76 % which is the highest level of probability.

Future studies in the Fethiye- Göcek Bay should concentrate on the depth-wise variations in the trace metal concentrations to have more information about the anthropogenic trace metal contamination. Since, As, Co, Cr and Ni are the elements having the most prominent effect in the unique ecosystem of Fethiye-Göcek Bay, the studies should be focused mostly on these metals.

CRediT authorship contribution statement

Conceptualization: Ö.A., U.A., Sampling: Ö.A., Sample Preparation: H.İ.G., E.T., Data curation: H.İ.G., Ş.A., Funding acquisition: Ö.A., Methodology, H.İ.G., E.T., U.A., Project administration: Ö.A.; Software: H.İ.G., Ş.A., Writing original draft: H.İ.G., Ş.A.; Review& editing, Ö.A., Ş. A., B.K.

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Declaration of competing interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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