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ORIGINAL ARTICLE

Spatial distribution of some elements and elemental contamination in the sediments of Köyceğiz Lake (SW Turkey)

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Abstract

Elemental accumulation, distribution and relationship profiles for sediment samples taken at 81 localities in the Köyceğiz Lake were investigated. Spatial distribution maps for ten elements (Cu, Pb, Zn, Ni, Cr, Co, Mn, Mo, Al, Fe) were created using the ordinary kriging interpolation method. Statistical tests revealed that the sediments taken from areas close to the Namnam (NamSM) and Kargıcak (KarSM) stream mouths have the highest element content. In addition, sediments close to NamSM have the highest contamination, according to contamination degree and modified contamination degree values. On the other hand, sediments close to KarSM have the highest value on the pollution load index. The enrichment factor and contamination factor values of Cr and Co, and especially Ni, close to NamSM are striking and have significantly higher values compared to the rest of the lake. There are strong correlations between these three elements, which were also confirmed by cluster analysis. Ni is the element having the highest value on the geoaccumulation index. In addition, according to the toxic unit results, it was found that 84–89% of the element-based toxic effect in the lake is due to Ni alone. According to the mean effect range median quotient values, the sediments of Köyceğiz Lake have a potential to show toxic effects of at least 76% in living organisms, which is due to the high levels of Ni. According to the mean probable effect low quotient value, it has been determined that Köyceğiz Lake is at a "highly impacted" level, which is the worst possible value on the quality scale.

Keywords Ecological risk · Pollution · Risk assessment · Sediment quality · Spatial distribution

Introduction

Recent studies have shown a trend in heavy metal contamination, especially in coastal areas, rivers and lakes (Wu et al. 2017; Zhang et al. 2017; Zhu et al. 2017). The trend in heavy metal contamination in many areas has been attributed to untreated disposal by industry, as well as from agricultural chemicals, settlements and mining (Eziz et al. 2018; Kinimo et al. 2018; Kusin et al. 2018; Rahman et al. 2014). The toxicity of heavy metals to aquatic organisms is in part related to metal persistence as well as concentration in the environment (Bakan and Özkoç 2007; He et al. 2009; Ismail and Beddri 2009; Nobi et al. 2010; Sany et al. 2013). From this perspective, it is important to analyze the sediments of an aquatic environment such as lakes, rivers and seas to evaluate the degree of heavy metal contamination. Analyzing sediments as a component of metal contamination is also important, because the suspended sediment particles in water transfer heavy metals from the surface to the bed sediment, thus becoming a potential source of contaminants in aquatic ecosystems (Ridgway and Shimmield 2005; Alexakis 2011). Almost 99% of discharged heavy metals precipitate in the sediments of the aquatic environments (Joksimovic et al. 2011; Rahman et al. 2014).

Metal contamination of aquatic ecosystems requires careful evaluation of geochemical datasets by applying specific contamination analyses methods. Since these methods compare the present metal concentrations with pre-industrial concentration levels (geochemical background), they can reveal anthropogenic metal contributions (Balik and Tunca 2015; El-Sorogy et al. 2016). Sites impacted by

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anthropogenic sources of metals may be compared to a background site to gauge aquatic life impacts attributed to human activities/pollutants.

In this study, sediment samples were collected at 81 different locations in Köyceğiz Lake. We evaluated elemental concentrations with two main objectives: (1) understanding the co-occurrence and accumulation of elements in a lacustrine environment and the accumulation relation between elements and (2) assessing the possible negative effect of the accumulated elements to the ecosystem.

Study area

Köyceğiz Lake (53 km^2) is located in Muğla province in the southwest of the Republic of Turkey (Fig. 1). The catchment area of Köyceğiz Lake (874 km^2) comprises different lithological units: (1) Quaternary alluvium (~ 170 km^2), (2) carbonaceous clastics (~ 40 km^2), (3) limestone (~ 120 km^2), (4) basalt (~ 44 km^2), and peridotite (~ 500 km^2) (Fig. 1) (Şenel 1997). Mafic and ultramafic igneous rocks cover almost 60% of the Köyceğiz catchment area. Weathering products from the lithological units are carried into the lake by three main inlets, namely Namnam, Kargıcak and Yuvarlak streams. However, the lake is discharged into the Mediterranean Sea through the Dalyan Channel (Fig. 1). The study area includes subaqueous and terrestrial hot and cold springs which affect the hydrogeochemical content of the aquatic systems (Avşar et al. 2017). Köyceğiz town (35,000 population) is the main settlement in the lake catchment. Citrus crops are the primary agricultural commodity and are farmed on Quaternary alluvium.

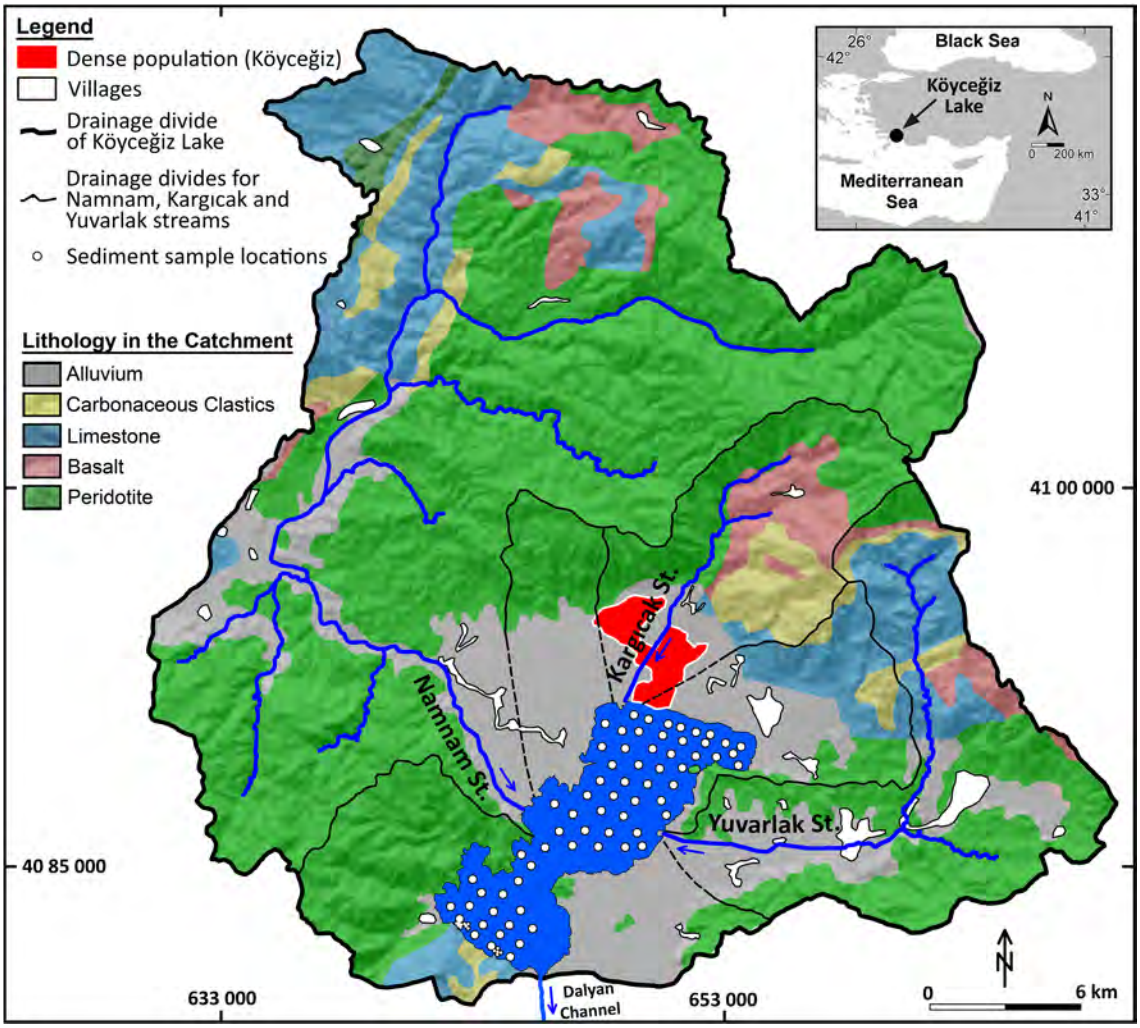


Fig. 1 Map showing the distribution of lithological units and settlements in the catchment of Köyceğiz Lake, as well as the sediment sampling locations within the lake (modified from Şenel 1997)

Materials and methods

Fieldwork

The sediment core samples acquired in 2014 for this study were taken from boat using a gravity corer at 81 locations. The corer, consisting of a 50 cm-long PVC pipe, was left to free fall approximately 2 m above the sediment/water interface. Soon after the PVC pipe penetrated the sediments, the corer was extracted. A vacuum system, used with the corer, enabled the sediments to be kept in the PVC pipe. The sediment cores were a minimum of 10 cm in length. The cores were stored in a cooling room at 4 °C until they were submitted for ICP–MS analysis. Only the top 5 cm of the sediments was used for element concentration analyses. For this study, 81 sediment samples from Köyceğiz Lake were analyzed (Fig. 1). Sixty-seven of the 81 sample localities were distributed randomly across the study area; 14 samples were concentrated near the subaqueous hot springs (SUB-1, SUB-2 and SUB-3) in the south of the lake.

The use of a gravity coring system for this study (rather than an Ekman sampler) was important because the sediment/water interface is not disturbed during gravity coring. This allowed the most recent, age-equivalent sediments to be sampled and analyzed for element contamination.

Element analyses

Sample preparation was completed in the Fatsa Faculty of Marine Sciences Research and Laboratory Center. Eighty-one samples were completely desiccated at 105 °C in a furnace. Dried samples were ground in a porcelain mortar, and approximately 100 g of sediment was sieved through a 63 µm mesh (El-Said et al. 2014; Omar et al. 2015). The amount of material coarser and finer than 63 µm was measured, and 2–3 g (min. 2 g) of material finer than 63 µm was separated for inductively coupled plasma–mass spectrometer (ICP–MS) analysis in an AQ270 packet (Acme Lab., Bureau Veritas Commodities Canada Ltd.).

The analysis of Mo, Cu, Pb, Zn, Ni, Co, Mn, Fe, As, Cd, Cr and Al elements was done using the ICP–MS method. Reference materials and duplicate measurements of three samples are presented in Table 1. Cd was not studied because the concentration of this element was below the detection limits of 0.5 ppm for Cd.

Table 1 Comparison of reference material values with measured values and measurement limits for elements

Method		AQ270										
Analyte		Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cr	Al
Unit		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	%
MDL		0.5	0.5	0.5	5.0	0.5	0.5	5.0	0.0	5.0	0.5	0.0
Pulp duplicates												
K27	Sediment pulp	8.0	35.5	10.7	48.0	697.8	49.7	573.0	3.1	< 5	197.8	1.2
K27	REP	8.5	35.3	10.5	52.0	699.6	51.9	551.0	3.1	< 5	195.6	1.2
K70	Sediment pulp	8.8	27.1	8.6	44.0	573.4	42.4	590.0	2.5	< 5	157.8	1.1
K70	REP	8.5	27.1	8.7	44.0	572.8	42.8	590.0	2.5	< 5	161.3	1.1
K-T-3-634	Sediment pulp	9.4	22.4	8.5	24.0	506.0	32.1	299.0	2.1	< 5	148.5	0.7
K-T-3-634	REP	9.2	21.0	8.1	23.0	484.9	29.5	291.0	2.0	< 5	141.0	0.6
Reference materials												
STD GBM398-4-AR	STD	929.6	3904.0	11945.5	5463.0	4217.6	2005.6	5261.0	3.9	6.0	1983.2	0.5
STD OREAS927-AR	STD	0.9	11015.7	220.0	752.0	27.1	30.6	1026.0	8.0	12.0	40.9	3.2
STD GBM398-4-AR	STD	948.3	4003.8	11895.2	5632.0	4225.4	2059.6	5285.0	3.7	6.0	2088.6	0.5
STD OREAS927-AR	STD	1.1	11039.6	222.4	769.0	30.3	29.6	1009.0	8.1	13.0	42.5	3.3
STD GBM398-4-AR	STD	940.7	3997.1	12043.1	5442.0	4256.1	2024.3	5311.0	3.9	6.0	2034.1	0.5
STD OREAS927-AR	STD	1.1	10870.7	236.5	756.0	29.7	28.8	1049.0	8.0	14.0	41.0	3.3
STD GBM398-4-AR	STD	927.6	3919.1	11747.9	5230.0	4180.6	2125.5	5240.0	3.9	7.0	2091.3	0.5
STD OREAS927-AR	STD	1.0	10750.9	190.9	694.0	27.3	27.5	991.0	7.9	12.0	38.9	3.1
STD GBM398-4-AR	STD	913.1	3968.7	11887.7	5462.0	4265.3	1975.3	5244.0	3.7	5.0	1966.0	0.5
STD OREAS927-AR	STD	1.2	10869.0	231.2	761.0	28.9	28.7	1084.0	8.0	12.0	40.4	3.1
STD GBM398-4-AR (expected)		917.0	3919.0	11750.0	5345.0	4135.0	1950.0	5300.0	4.0	6.0	1950.0	0.48
STD OREAS927-AR (expected)		1.1	10715.0	232.0	726.0	30.9	29.4	1110.0	8.2	13.5	41.7	3.3

Ordinary kriging

To visualize the spatial distribution of elements in the study area, interpolation maps were created for the studied elements utilizing a conventional Kriging method with the help of the Geostatistical Analyst module of ArcGIS 10.2.1 computer program. The interpolation maps were prepared using equal variogram parameters such as nugget effect, range and sill. Kriging surfaces are useful for showing the geographical distribution of anomalously high, moderate and low element concentrations.

Contamination analyses

Most of the techniques for element contamination evaluation compare the concentration of element in the modern sediments with the concentrations from the pre-industrial period. This type of evaluation can be used to assess anthropogenic influx of contaminants that are toxic to aquatic organisms. The contamination investigation techniques can be categorized into three groups as indicated by the proposed analysis methods; (1) those revealing the amount of anthropogenic pollution in sediments, (2) those investigating the effect of sediment pollution on ecosystems and (3) those presenting the reference and/or limit values (Balik and Tunca 2015). The most widely used reference values are the ones presented by Turekian and Wedepohl (1961). The parameters and their calculation methods used to evaluate the element contamination in Köyceğiz Lake are presented below.

Contamination factor (C_f^i)

The contamination factor (C_f^i) was first introduced by Hakanson (1980) to evaluate the anthropogenic element contamination in sediments. The method fundamentally makes a comparison between the present concentrations and the concentration of the reference baseline value of the pre-industrial time. C_f^i is calculated by Eq. 1, and ranges for C_f^i classes are presented in Table 2.

$$C_f^i = \frac{C_i}{C_n}, \tag{1}$$

where C_i is the amount of the element and C_n is the reference value of the element [average crustal abundance was used as a reference (Turekian and Wedepohl 1961)].

Contamination degree (Cd)

Contamination degree (Cd) was aslo presented by Hakanson (1980), and this strategy computes the anthropogenic element contamination in sediments. This method sums the total element concentrations, and the formula for (Cd) is written below (Eq. 2). The ranges for Cd classes are also presented in Table 2.

$$\text{Cd} = \sum_{i=1}^{n} C^i f, \tag{2}$$

where $C^i f$ is the contamination factor.

Modified contamination degree (mCd)

Abrahim and Parker (2008) modified the equation for contamination degree (C_d) by dividing the contamination degree by the quantity of the elements; using an average, the value is established using Eq. 3. The ranges for mCd classes are presented in Table 2.

$$\text{mCd} = \frac{\sum_{i=1}^{n} C^i f}{n}, \tag{3}$$

where $C^i f$ is the contamination factor and n is the number of elements analyzed.

Enrichment factor (EF)

The enrichment factor (EF) is another commonly utilized index for detecting anthropogenic element contamination in the sediments. This method aims at detecting the human effect on element contamination by taking elements such as Al and Fe as reference. Al and Fe are used as reference, since these elements are abundant in the aquatic environment and less affected by contamination. Fe was utilized in this study as the reference element (Sallam et al. 2015; Zhu et al. 2017). The classification ranges for EF, which can be calculated with Eq. 4, are presented in Table 2.

$$\text{EF} = \frac{\frac{C_n}{C_\text{ref}}}{\frac{B_n}{B_\text{ref}}}, \tag{4}$$

where C_n is the quantity of the elements, C_ref is the value of the studied element in the reference sample (e.g., the Earth's crust), B_n is the value of the reference element in the studied sample (e.g., Fe or Al) and B_ref is the value of the reference element in the reference sample.

Geoaccumulation index (Igeo)

Another method used to evaluate the anthropogenic element contamination in the sediments calculates the geoaccumulation index (Igeo), which was initially proposed by Müller (1969). Igeo can be obtained using Eq. 5, and the ranges for the Igeo classes are presented in Table 2.

Table 2 Scales showing the levels established for the sediment assessment methods used

	Cu	Pb	Zn	Ni	As	Cr
ERM (freshwater)	390	110	270	50	85	145
PEL (freshwater)	197	91.3	315	36	17	90
TEL (freshwater)	35.7	35	123	18	5.9	37.3
ERL (freshwater)	70	35	120	30	33	80
Earth's crust	45	20	95	68	13	90
Contamination degree (Cd)						
Cd < 8	8 ≤ Cd ≤ 16	16 ≤ Cd ≤ 32	Cd ≥ 32			
Low	Moderate	Considerable	Very high			
Contamination factor (C_f^i)						
$C_f^i < 1$	$1 \leq C_f^i < 3$	$3 \leq C_f^i > 6$	$C_f^i \geq 6$			
Respectively low	Moderate	Considerable	Very high			
Modified contamination degree (mCd)						
mCd < 1.5	1.5 ≤ mCd < 2	2 ≤ mCd < 4	4 ≤ mCd < 8	8 ≤ mCd < 16	16 ≤ mCd < 32	mCd ≥ 32
Nil to very low	Low	Moderate	High	Very high	Extremely high	Ultra high
Enrichment factor (EF)						
EF < 2	2 ≤ EF < 5	5 ≤ EF < 20	20 ≤ EF < 40	EF ≥ 40		
Minimal	Moderate	Significant	Very high	Extremely high		
Geoaccumulation index (Igeo)						
Igeo ≤ 0	0 < Igeo < 1	1 < Igeo < 2	2 < Igeo < 3	3 < Igeo < 4	4 < Igeo < 5	Igeo ≥ 5
Practically uncontaminated	Uncontaminated to moderately	Moderately	Moderately to strongly	Strongly	Strong to extremely	Extremely
Pollution load index (PLI)						
0	1	> 1				
Perfection	Baseline	Deterioration				
Potential ecologic risk factor (ERi)						
ERi < 40	40 ≤ ERi < 80	80 ≤ ERi < 160	160 ≤ ERi < 320	320 ≥ ERi		
Low	Moderate	Considerable	High	Very high		
m-PEL-Q						
m-PEL-Q < 0.1	0.1 < m-PEL-Q < 1	m-PEL-Q > 1				
Unimpacted	Moderately impacted	Highly impacted				
m-ERM-Q						
m-ERM-Q < 0.1	0.11 < m-ERM-Q < 0.5	0.51 < m-ERM-Q < 1.5	m-ERM-Q > 1.5			
%9 toxic	%21 toxic	%49 toxic	%76 toxic			

PEL probable effect level, *TEL* threshold effect level (Smith et al. 1996), *ERM* effect range median, *ERL* effect range low (Long and Morgan 1991)

Earth crust's values (Turekian and Wedepohl 1961)

$$\mathrm{Igeo} = \log 2\left(\frac{C_n}{1.5 \times B_n}\right), \tag{5}$$

where C_n is the quantity of the studied elements, B_n is the element concentration in the studied sample and 1.5 is the natural oscillation coefficient

Pollution loading index (PLI)

The pollution loading index (PLI), which can be calculated with Eq. 6, was introduced by Tomlinson et al. (1980) to compare the anthropogenic element contamination in sediments for different locations. The classification ranges for PLI can be found in Table 2.

$$\mathrm{PLI} = (Cf1 \times Cf2 \times Cf3 \times \ldots\ldots Cfn)^{\frac{1}{n}}, \tag{6}$$

where C_f is the contamination factor and n is the quantity of the studied elements.

Potential ecologic risk factor (ERi)

The potential ecologic risk factor, first utilized by Hakanson (1980), which can be calculated using Eq. 7, has been used to demonstrate the impact of element contamination on organisms and on ecosystems. The classification ranges for ERi can be found in Table 2.

$$E^i r = \frac{T^i r \times C^i}{Co}, \tag{7}$$

where $T^i r$ is the toxic response factor, C^i is the amount of element in samples and C_0 is the reference value of the element.

Mean effect range-median quotient (m-ERM-q) and mean probable effect level quotient (m-PEL-q) methods

m-ERM-q and *m-PEL-q* indices are useful for understanding the effect of element contamination in sediments on ecosystems using the effect range median (ERM) values and probable effect level (PEL) values (Table 2). The formulas are given below (Eqs. 8 and 9).

$$\text{m-ERM-Q} = \sum_{i=1}^{n} \frac{\frac{C_i}{\mathrm{ERM}_i}}{n}, \tag{8}$$

where C_i is the value of the studied element in the samples, ERM is the influence interval value of the studied element and N is the quantity of the studied elements.

$$\text{m-ERM-Q} = \sum_{i=1}^{n} \frac{\frac{C_i}{\mathrm{PEL}_i}}{n}, \tag{9}$$

where C_i is the value of the studied element in the samples, PEL is the average possible level of the effect value of the studied element and N is the quantity of the studied elements

Toxic unit sum (ΣTUs) and proportional toxic unit (proportional TU)

The toxic unit sum (ΣTUs) and proportional toxic unit (proportional TU) indices demonstrate the impact of the element contamination in sediments. The proportional TU can be calculated by using the values of ΣTUs. These indices are calculated by Eqs. (10 and 11).

$$\sum \mathrm{TUs} = \sum_{i=1}^{n} \frac{C_i}{\mathrm{PEL}_i}, \tag{10}$$

where Ci is the amount of the studied element in the samples, PELC_i is the PEL (probable effect level) value of the studied element and N is the quantity of the studied elements.

$$\text{Proportional TU} = \left(\frac{\frac{C_i}{\mathrm{PEL}_i}}{\Sigma\mathrm{TUs}}\right). \tag{11}$$

Statistical methods

Before comparison of the means and correlation analyses, the Shapiro–Willk test was used to identify the distribution of the data. This test is useful for evaluating small data sets (Aydin et al. 2014). Since the distribution was not parametric, the Kruskal–Wallis test and Mann–Whintney *U* test from the comparison tests were utilized, and the Spearman correlation analysis was used as the correlation analysis method (Aydın et al. 2017). In cases where the data were insufficient to be identified as normally distributed, tests were used regardless of the distribution (Tunca et al. 2016). Cluster analysis (CA) was used after z-score correction via Euclidean distance according to the Ward method (Üçüncü Tunca et al. 2016). All statistical analyses were performed with SPSS v. 21 (IBM, USA).

Results and discussion

Current element level in the lake and intermetallic relationships

The coordinates of 81 sediment sampling locations and the results of ICP–MS analysis on these samples are presented in Table 3. The results show that there are some differences between the areas of stream inlets and the

Table 3 ICP–MS analysis results of 81 sediment samples

#	Sample ID	*X*	*Y*	Mo (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	Fe (%)	Cr (mg/kg)	Al (%)
1	K-1	648,955	4,090,607	5.4	49.0	11.7	64	675.7	51.0	653	3.69	199.3	1.67
2	K-2	648,150	4,089,979	7.5	37.6	12.2	52	644.0	48.8	693	3.09	189.2	1.30
3	K-3	646,262	4,087,710	2.2	46.8	8.2	53	1476.2	90.7	976	5.10	388.2	1.39
4	K-5	644,934	4,085,676	3.0	44.2	7.3	55	1278.1	79.4	850	4.68	391.4	1.34
5	K-6	643,321	4,084,181	8.0	26.1	7.6	36	648.9	38.9	362	2.49	194.8	0.87
6	K-7	642,862	4,083,653	8.1	25.0	6.9	30	554.2	34.9	314	2.20	165.2	0.80
7	K-9	642,097	4,083,621	7.7	24.5	6.3	29	604.1	33.4	267	2.34	167.0	0.81
8	K-10	643,798	4,083,413	12.3	27.8	9.6	37	535.4	34.4	338	2.13	170.3	0.80
9	K-11	644,188	4,084,101	3.3	29.3	8.9	43	812.6	62.6	1011	3.14	266.3	1.07
10	K-12	644,828	4,084,650	12.6	27.8	9.4	39	708.9	44.1	403	2.67	217.5	0.94
11	K-13	645,320	4,085,261	0.6	32.9	7.6	43	1002.7	66.4	922	3.45	295.2	0.94
12	K-14	645,876	4,085,956	0.0	41.3	6.7	52	1466.3	94.4	1185	4.67	371.1	1.09
13	K-15	646,450	4,086,636	0.0	41.0	7.0	52	1768.2	108.5	1003	5.40	439.8	1.11
14	K-16	646,992	4,087,300	1.0	42.5	7.0	54	1527.7	89.1	792	5.08	407.6	1.25
15	K-17	647,583	4,088,032	9.4	33.9	8.2	44	761.3	47.6	549	2.99	221.5	1.06
16	K-18	648,079	4,088,632	7.8	37.7	10.6	53	791.8	56.6	621	3.29	210.4	1.30
17	K-19	648,575	4,089,249	7.9	33.6	9.7	48	610.4	46.3	543	2.77	180.5	1.15
18	K-20	649,088	4,089,900	6.6	33.0	10.2	45	548.5	45.6	534	2.63	156.9	1.13
19	K-21	649,632	4,090,562	0.8	77.4	12.7	79	828.3	64.2	929	5.10	296.4	2.31
20	K-22	648,280	4,090,888	4.2	50.1	12.2	68	766.6	56.7	956	3.97	248.2	1.70
21	K-23	650,589	4,090,434	2.9	68.7	12.8	71	782.5	61.3	767	4.49	266.0	2.03
22	K-24	650,173	4,089,890	1.2	92.8	13.3	83	866.1	65.3	969	5.24	300.1	2.38
23	K-25	649,609	4,089,254	5.1	58.0	13.7	72	673.0	51.0	728	3.97	219.2	1.80
24	K-26	649,064	4,088,587	10.3	32.1	9.1	45	616.8	44.0	537	2.68	172.6	1.10
25	K-27	648,616	4,088,021	8.0	35.5	10.7	48	697.8	49.7	573	3.06	197.8	1.19
26	K-28	648,103	4,087,422	6.7	40.9	10.2	50	1062.5	68.1	690	3.92	286.1	1.26
27	K-29	647,464	4,086,657	1.9	42.9	8.8	53	1398.5	86.6	991	4.86	389.6	1.27
28	K-30	646,970	4,086,044	0.5	39.7	7.4	51	1716.7	109.2	1119	5.31	443.8	1.15
29	K-34	644,873	4,083,484	10.7	26.6	6.9	32	602.6	41.3	431	2.27	185.8	0.81
30	K-35	644,430	4,082,925	11.9	26.5	7.0	31	531.2	33.7	336	2.10	166.3	0.78
31	K-36	644,081	4,082,513	12.8	33.1	9.1	43	705.6	44.6	440	2.77	218.5	1.00
32	K-37	643,718	4,082,070	14.1	27.2	7.0	32	594.5	36.3	365	2.29	174.0	0.85
33	K-38	643,387	4,082,903	13.7	26.5	6.7	30	577.9	33.6	331	2.17	167.9	0.79
34	K-39	643,071	4,082,508	10.6	25.8	8.9	32	520.3	33.0	513	2.14	163.0	0.81
35	K-40	642,452	4,083,142	10.0	22.5	6.2	27	463.5	27.5	305	1.88	142.9	0.67
36	K-41	642,996	4,084,726	8.0	25.3	8.7	30	650.9	38.4	318	2.46	186.8	0.75

Table 3 (continued)

#	Sample ID	*X*	*Y*	Mo (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	Fe (%)	Cr (mg/kg)	Al (%)
37	K-42	644,494	4,081,634	7.1	25.9	10.2	37	548.6	34.4	446	2.31	192.4	0.88
38	K-43	644,872	4,082,142	5.0	23.0	7.1	29	475.3	28.1	405	1.89	149.7	0.74
39	K-44	645,379	4,082,750	4.5	26.9	7.7	32	607.4	39.7	483	2.49	195.1	0.96
40	K-47	648,001	4,086,000	0.0	25.3	7.6	41	919.7	63.9	2146	3.54	279.4	1.01
41	K-48	648,447	4,086,580	3.2	41.2	7.4	55	1209.7	78.6	1017	4.59	356.2	1.37
42	K-49	648,992	4,087,228	6.2	38.8	8.2	57	874.0	63.4	673	3.64	243.3	1.37
43	K-50	649,472	4,087,826	7.6	39.4	10.0	57	824.6	58.4	693	3.71	231.2	1.48
44	K-51	650,001	4,088,492	9.4	27.9	11.0	41	560.1	41.8	524	2.42	152.0	1.03
45	K-52	650,482	4,089,108	7.7	33.6	9.8	50	634.8	49.8	570	2.89	179.8	1.26
46	K-53	650,932	4,089,676	8.9	29.8	9.1	42	568.6	43.5	536	2.51	159.4	1.11
47	K-54	651,381	4,090,220	8.4	35.1	10.1	58	596.7	47.8	606	3.00	162.9	1.39
48	K-55	652,306	4,090,116	7.0	26.8	8.2	41	488.3	37.0	591	2.34	139.6	1.09
49	K-56	651,919	4,089,598	8.6	30.9	8.9	43	623.9	42.2	594	2.83	183.9	1.19
50	K-57	651,356	4,089,125	7.1	29.6	9.6	44	666.2	41.9	660	2.96	201.5	1.19
51	K-58	651,018	4,088,464	7.7	33.1	11.4	48	701.3	51.4	721	3.09	198.7	1.28
52	K-59	650,504	4,087,831	10.5	33.7	8.8	50	760.3	53.0	733	3.17	210.8	1.28
53	K-61	649,544	4,086,587	0.0	32.3	7.6	53	914.2	65.3	1519	4.15	273.5	1.43
54	K-62	649,048	4,085,973	0.0	19.4	6.6	32	647.1	42.9	1466	2.62	195.9	0.88
55	K-67	649,761	4,086,044	0.0	23.4	9.0	43	744.9	54.1	1637	3.29	221.9	1.12
56	K-68	650,723	4,087,255	0.0	27.7	9.7	48	850.2	61.9	2748	3.73	257.3	1.24
57	K-70	652,739	4,089,574	8.8	27.1	8.6	44	573.4	42.4	590	2.48	157.8	1.07
58	K-71	653,093	4,090,108	3.3	25.5	9.4	44	462.1	35.3	921	2.30	146.1	1.04
59	K-72	653,719	4,089,989	3.7	29.7	11.1	51	538.8	41.8	1215	2.68	185.1	1.19
60	K-73	653,410	4,089,703	5.7	24.8	9.8	43	470.3	36.2	687	2.19	147.7	0.99
61	K-74	653,614	4,089,248	2.6	29.8	11.0	48	560.4	45.4	1153	2.67	190.0	1.10
62	K-75	649,456	4,091,218	0.0	76.6	11.3	78	850.6	62.4	1075	5.25	295.5	2.28
63	K-76	650,035	4,091,048	3.7	69.1	15.1	80	759.0	57.6	834	4.70	267.1	2.10
64	K-77	650,813	4,090,888	4.2	34.1	11.0	56	472.5	36.4	684	2.86	153.3	1.40
65	K-78	651,312	4,090,737	0.8	65.8	24.9	116	205.1	30.4	800	4.67	98.5	2.73
66	K-79	651,919	4,090,534	2.2	41.6	15.0	73	322.2	33.5	736	3.18	114.2	1.78
67	K-80	652,488	4,090,455	4.3	29.7	9.6	49	419.6	34.5	823	2.61	139.3	1.26
68	K-R-027	643,975	4,081,886	9.8	31.7	7.5	44	623.8	43.8	472	2.59	201.5	1.09
69	K-R-618	644,120	4,081,843	10.5	29.5	7.4	38	611.2	39.2	429	2.52	197.2	1.04
70	K-R-619	643,861	4,081,923	10.4	25.6	6.5	34	512.0	30.9	353	2.14	166.2	0.91
71	K-R-620	643,987	4,082,011	7.2	16.2	5.1	34	354.0	22.6	249	1.49	108.2	0.52

Table 3 (continued)

#	Sample ID	X	Y	Mo (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	Fe (%)	Cr (mg/kg)	Al (%)
72	K-R-621-Y	643,940	4,081,750	4.7	26.3	10.0	54	635.6	44.0	1040	2.99	197.7	1.21
73	K-T-3-000	642,725	4,082,889	9.7	21.8	7.2	49	551.3	36.7	578	2.22	168.7	0.83
74	K-T-3-631	642,795	4,082,968	10.1	22.0	7.4	36	541.1	31.4	296	2.26	146.3	0.69
75	K-T-3-633	642,804	4,082,807	9.0	18.7	8.6	22	398.9	24.7	244	1.59	116.1	0.55
76	K-T-3-634	642,663	4,082,973	9.4	22.4	8.5	24	506.0	32.1	299	2.11	148.5	0.68
77	K-015-000	642,409	4,082,916	4.4	31.7	11.9	48	685.4	51.8	972	2.99	221.0	1.18
78	K-015-638	642,491	4,082,865	6.1	21.3	8.0	31	468.6	31.8	407	1.98	152.9	0.72
79	K-015-643	642,514	4,082,948	12.2	25.8	7.1	32	533.9	33.9	279	2.14	161.3	0.77
80	K-015-645	642,428	4,083,010	6.5	24.9	9.0	36	512.6	35.5	293	2.12	147.7	0.71
81	K-015-647	642,325	4,082,985	15.0	23.8	6.8	30	483.3	28.5	270	1.82	139.0	0.65

rest of the lake in terms of the sediment element concentrations. This difference is seen both in element concentrations that accumulate in the sediment and in the interrelationships between metals. For this reason, the element concentrations in the sediments were evaluated separately for the entire lake and for four sub-regions, namely, at stream inlets including: (1) Namnam Stream mouth, (NamSM), (2) Kargıcak Stream mouth, (KarSM), (3) Yuvarlak Stream mouth (YuvSM) and (4) the southwestern part of the lake where subaqueous hot springs are located (HotSR).

Kriged surfaces displayed on maps were used to show sediment element concentrations (Fig. 2a–j). In Table 4, descriptive statistics of elemental concentrations for the entire lake and the four sub-regions are presented. Accordingly, the region with the highest amount of elements accumulation in the lake is NamSM, followed by KarSM. Element concentrations in the sediments taken from YuvSM and HotSR are relatively low. The amount of mean elemental concentration for the entire lake is intermediate between the elemental concentration values in the four sub-regions. The sediment in Köyceğiz Lake has significantly higher concentrations of Cr and Ni (Table 4). It is well known that the chemical weathering products of mafic and/or ultramafic rocks are expected to be rich in clay minerals, and elements such as Cr and Ni (e.g., Wronkiewicz and Condie 1989). Since peridotite and basalt cover almost 60% of the catchment of Köyceğiz Lake (Fig. 1), we attribute the source of high Cr and Ni concentrations in the sediments to the weathering of these rocks.

Sediment evaluation methods yield a similar picture. The degree of contamination (cd), modified degree of contamination (mCd) and pollution load index (PLI) were used to compare KarSM, NamSM, as well as the entire lake (Tables 5, 6, 7). These methods are commonly used to compare the general state of elements in multiple areas (Zhao et al. 2015; Alshahri 2017). Accordingly, the areas with the highest contamination indices are NamSM and KarSM, but the region that has higher contaminations varies according to the method used. According to Cd and *mCd* values, NamSM (34.09 and 3.41, respectively) is more contaminated than KarSM (21.45 and 2.15, respectively). These values put NamSM at a level of ‘very high contamination’ (yhe contamination scale is given on Table 2), which is the highest value on the scale; KarSM at a level of ‘considerable contamination’, which is the second highest value on the scale. The reason why Cd gives such high results is largely due to the high contamination factor value of Ni. Since Cd is the sum of the contamination factor values of the elements being studied, Ni dominates the results. The arithmetic average of Cd and mCd, on the other hand, reveals a slightly more optimistic picture. Since the high contamination factor value of Ni occurs in the arithmetic average, its predominant

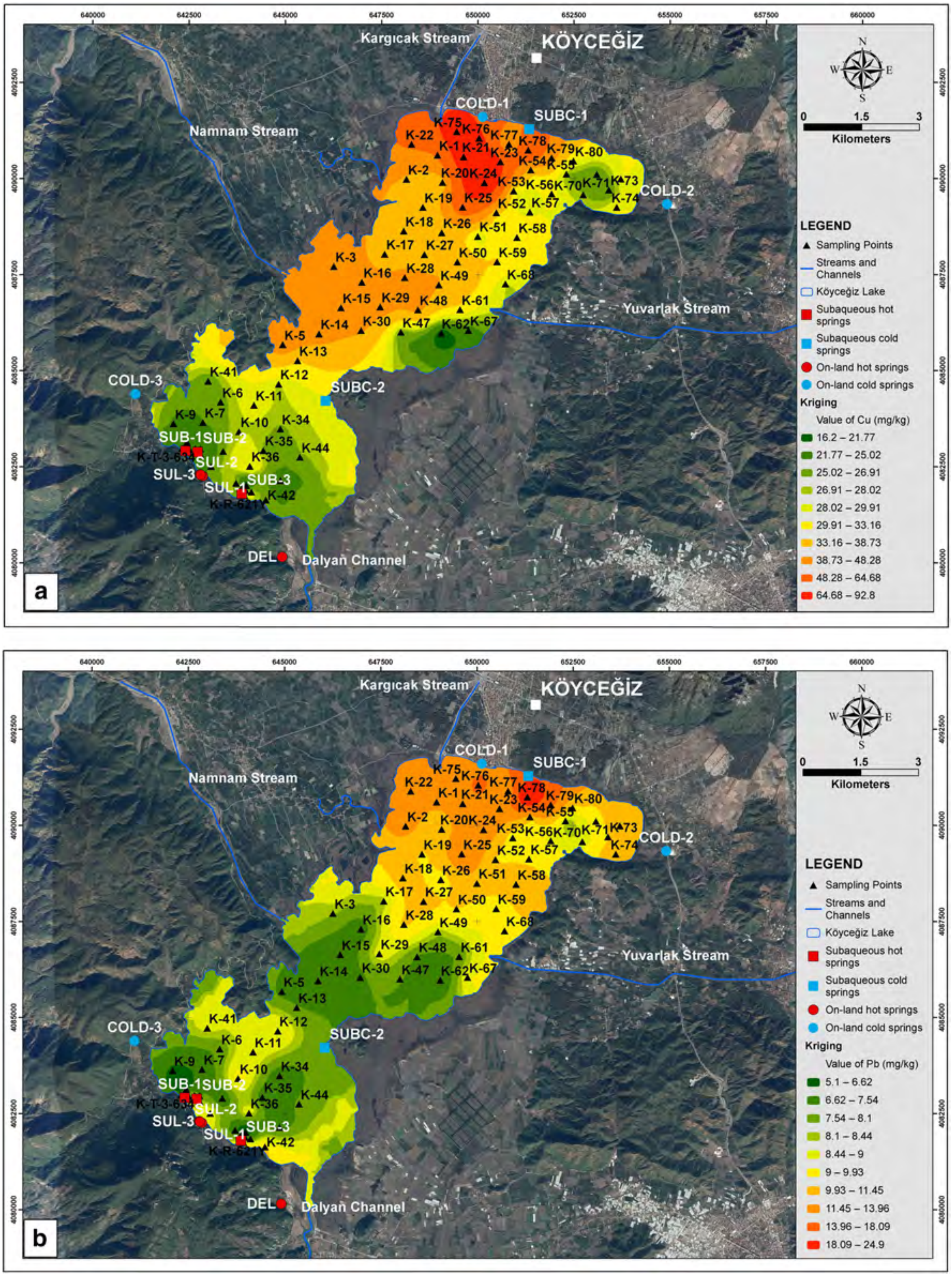


Fig. 2 Spatial distribution of ten elements in the sediments of Köyceğiz Lake: **a** Cu, **b** Pb, **c** Zn, **d** Ni, **e** Cr, **f** Co, **g** Mn, **h** Mo, **i** Al and **j** Fe

effect on the overall data is relatively small. According to the results of mCd, both regions are moderately contaminated.In the comparison based on PLI values, the results for NamSM and KarSM are similar, but KarSM has a slightly higher value than NamSM (1.13 and 0.98, respectively). When we consider that the deterioration initiation value, which is the

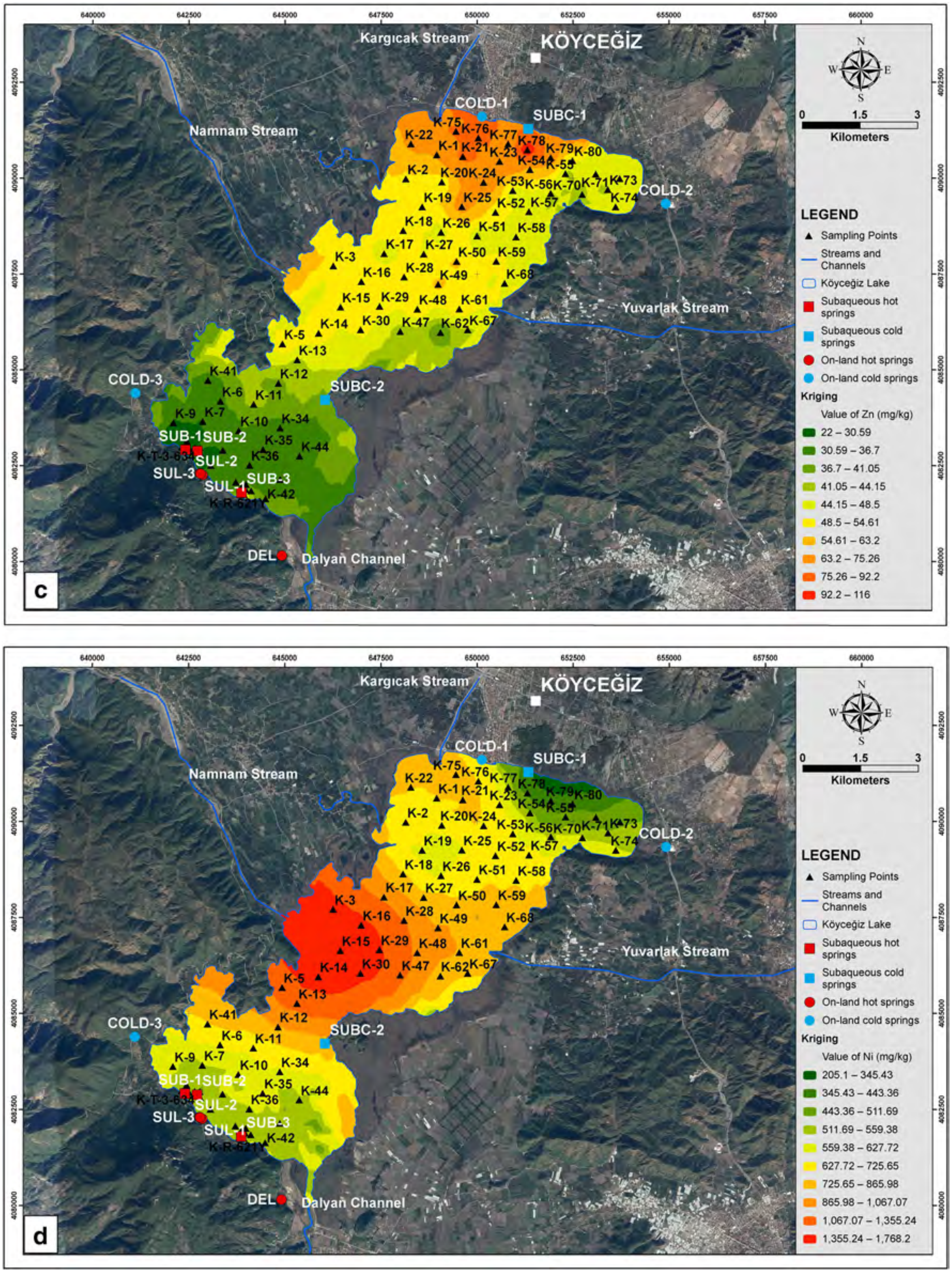
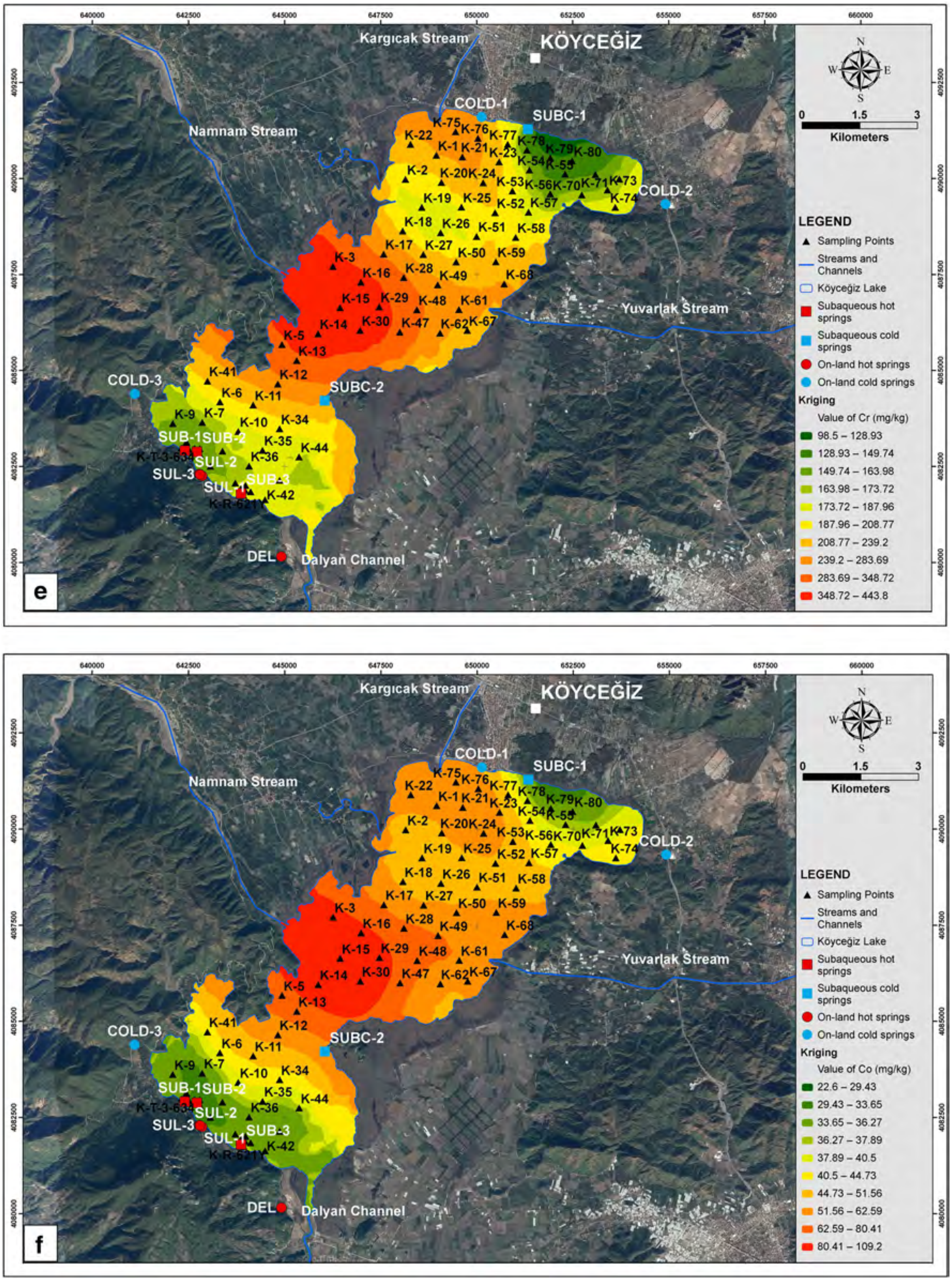


Fig. 2 (continued)



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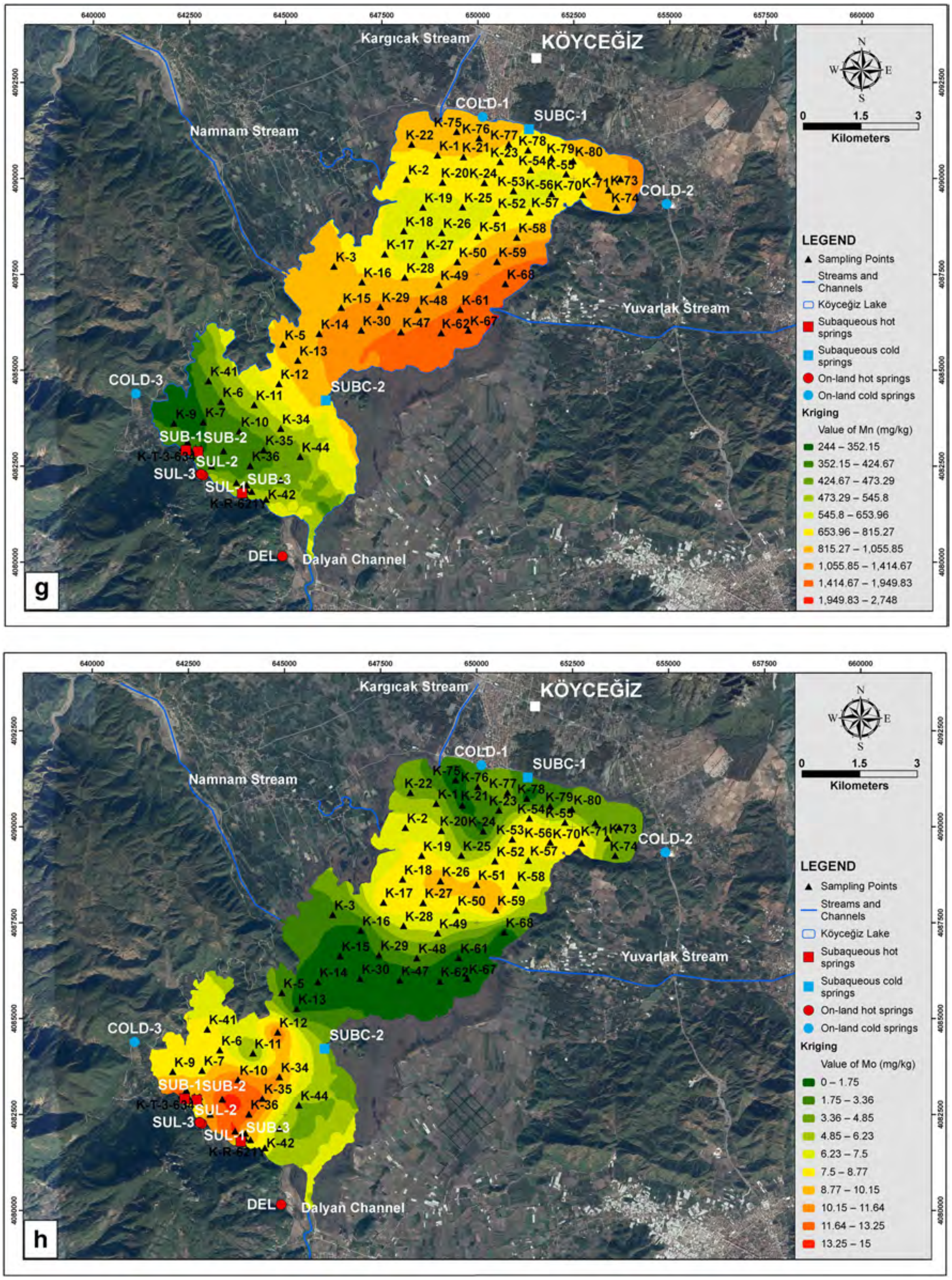

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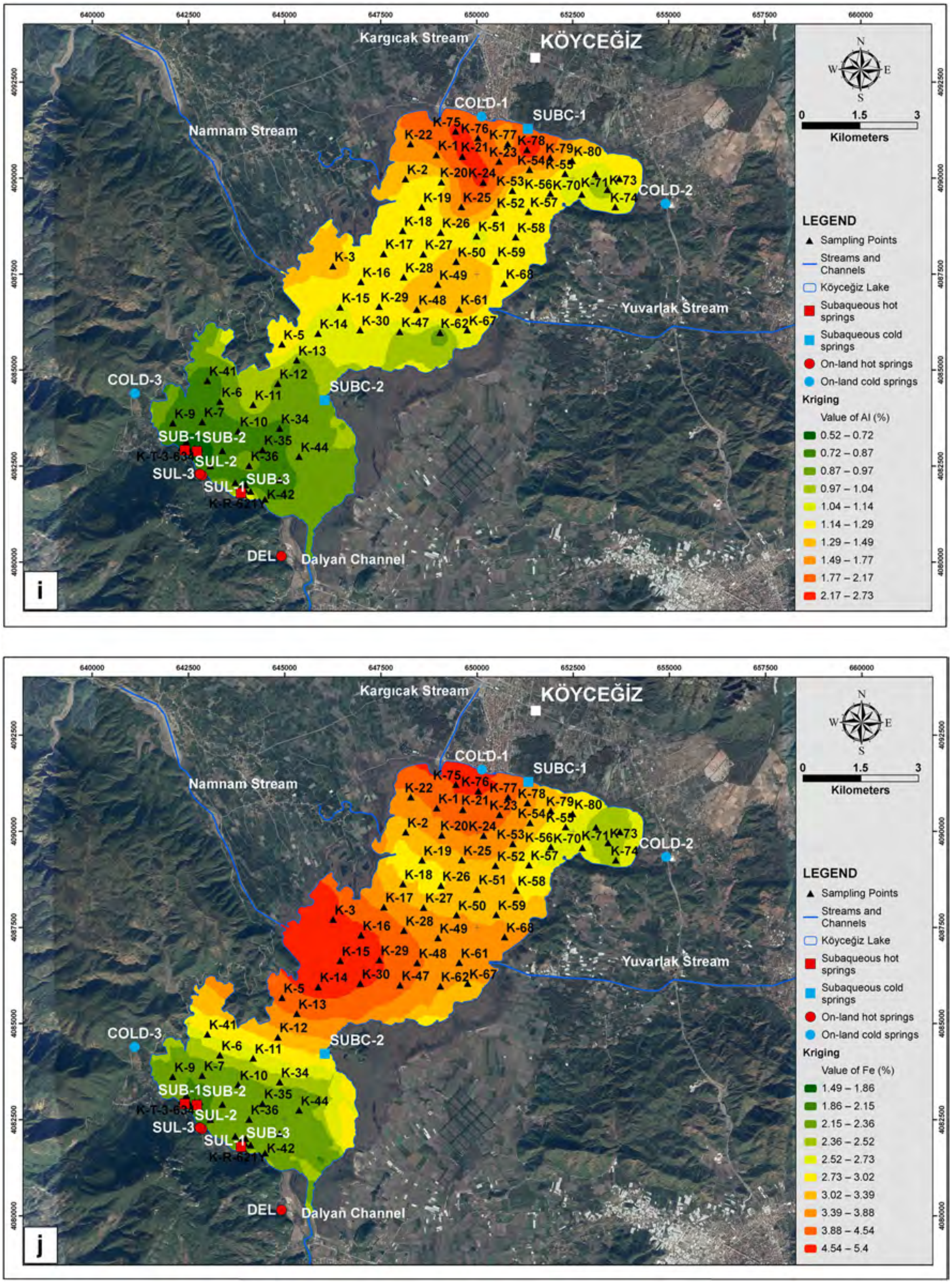

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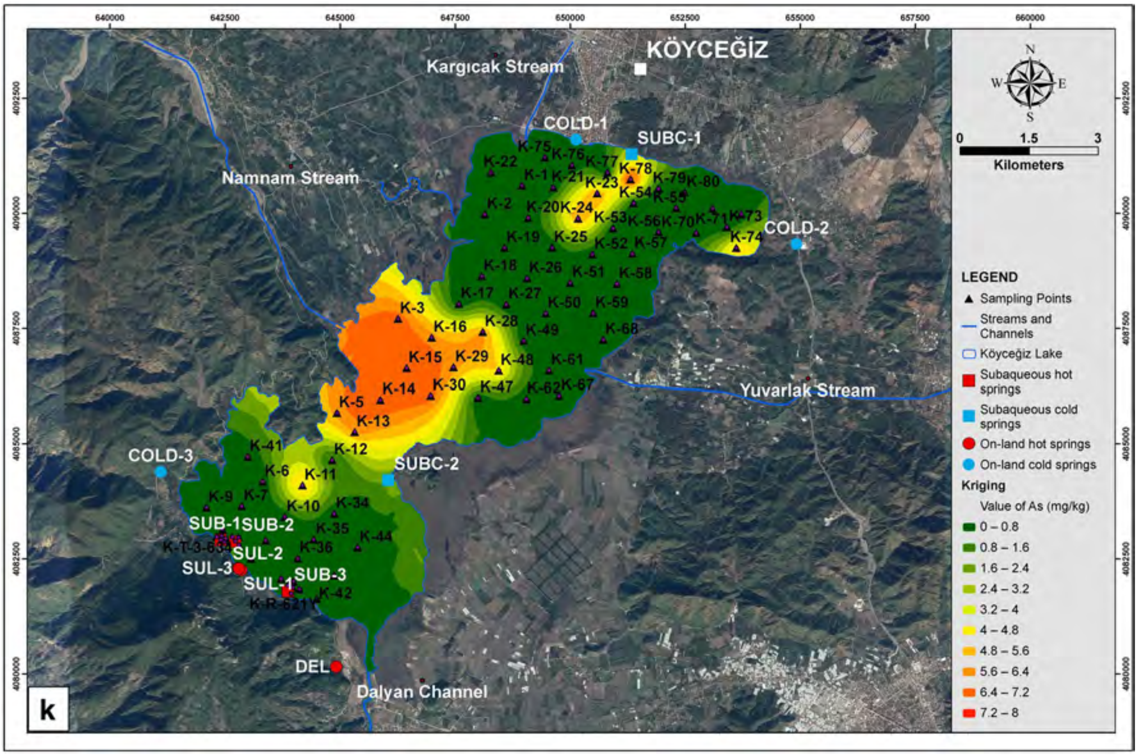

Fig. 2 (continued)

critical level for PLI = 1, the values obtained are at the upper limit. Similarly, the PLI value for the entire lake is 0.90, which indicates a severe contamination and at the upper limit of the contamination scale.

When we evaluated the general profile of the ten elements studied together with accumulation differences, it is seen that the strongest correlation is between Cr and Ni ($r = 0.965$) (Table 8). Other significant correlations were observed between Co and Ni ($r = 0.934$), and Cr and Co ($r = 0.907$). Strong correlations can also be seen between these elements on the kriged surface maps (Fig. 2a–j). Cluster analysis (CA) results are consistent with correlation analysis results. In the dendrogram, Ni, Cr and Co are in a single cluster and show the strongest relationship (Fig. 3). When we look at the distance proximity matrix of CA, it can be seen that the closest distances are between these three elements (Table 9): Cr–Ni (Euclidian distance = 2.10), Co–Ni (Euclidian distance = 2.33), and Cr–Co (Euclidian distance = 2.43). The strong correlation between Cr, Co and Ni, and the accumulation levels in the sediments reveal the possibility of either an anthropogenic or rock (ultramafic) source, which is also supported by the EF values, with reference to the Earth crust values (Tables 5, 6, 7).

Cr–Co and Ni show elevated concentrations in lake sediments when compared with crustal abundances (Tables 5, 6, 7). The contamination factor (C_f^i) values of these three elements (Ni = 20.45, Co = 4.58, Cr = 4.19) in NamSM are higher than in other parts of the lake. These values are ‘very high’ for Ni ($Cfi \geq 6$), which is the highest value in the classification, and ‘considerable’ ($3 \leq Cfi > 6$) for Co and Cr. EF (Ni = 18.85, Co = 4.22, Cr = 3.86) and geoaccumulation index (Igeo) (Ni = 3.75, Cr = 1.47, Co = 1.59) results also support the C_f^iresults. Different scales are used in the interpretation of the enrichment factor (EF*)*. According to the first scale, a level of 1.5 indicates an anthropogenic source, and Ni, Co and Cr are well above this limit (Zhang and Liu 2002). In the five-stage scale developed by Haris and Aris, Ni shows strong accumulation, and Cr and Co show moderate accumulation (Haris and Aris 2012). According to the shown values, there is a strong contamination of Ni, which is the fifth level of the seven-level scale, and moderately contaminated for Co and Cr, which is the third level of the same scale (Tomlinson et al. 1980).

Another pair of elements with very high correlation values within the lake sediments is Al and Zn (Al–Zn $r = 0.943$). The strong relationship between these two elements is also supported by cluster analysis. These two elements were located in the same cluster in the cluster analysis (Fig. 3) and showed very close proximity in the proximity matrix with an Euclidian distance of 2.47 (Table 9). This is the second closest distance after the Cr–Ni–Co triple. When

Table 4 The values of the studied elements, the limit values of these elements according to sediment quality guidelines and the comparison of these values of the studied elements

	Mo (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	Fe (%)	As (mg/kg)	Cr (mg/kg)	Al (%)
Entire lake (a)											
Mean	$6.30^{d,e}$	34.38^{e}	$9.29^{b,d,e}$	46.93^{e}	712.81^{c}	48.88^{c}	713.35	3.09^{e}	$1.30^{c,d,e}$	$212.45^{c,e}$	$1.17^{b,e}$
Std	3.99	14.10	2.72	15.49	301.29	18.44	418.66	1.02	2.56	77.55	0.43
Min	0.00	16.20	5.10	22.00	205.10	22.60	244.00	1.49	0.00	98.50	0.52
Max	15.00	92.80	24.90	116.00	1768.20	109.20	2748.00	5.40	8.00	443.80	2.73
Namnam Stream mouth (NamSM) (b)											
Mean	$2.08^{c,e}$	42.05	$7.84^{a,d,e}$	52.00^{e}	1366.61	85.25	$940.20^{c,e}$	4.69^{c}	6.30	371.34	$1.24^{a,e}$
Std	1.99	3.92	1.05	3.50	230.84	12.60	136.60	0.59	0.67	47.84	0.15
Min	0.00	32.90	6.70	43.00	1002.70	66.40	690.00	3.45	5.00	286.10	0.94
Max	6.70	46.80	10.20	55.00	1768.20	108.50	1185.00	5.40	7.00	439.80	1.39
Kargıcak Stream mouth (KarSM) (c)											
Mean	$2.63^{b,e}$	64.91	14.27	78.40	$672.91^{a,e}$	$53.34^{a,e}$	$844.70^{b,e}$	4.43^{b}	$2.00^{a,d,e}$	$230.45^{a,e}$	2.08
Std	1.92	15.52	3.94	14.45	226.84	12.32	132.63	0.70	3.27	73.32	0.35
Min	0.00	41.60	11.30	64.00	205.10	30.40	653.00	3.18	0.00	98.50	1.67
Max	5.40	92.80	24.90	116.00	866.10	65.30	1075.00	5.25	8.00	300.10	2.73
Hot spring area (HotSR) (d)											
Mean	$8.71^{a,e}$	23.87	$8.45^{a,b,e}$	36.20	531.67	35.04	467.80	2.22	$1.10^{a,c,e}$	159.92	0.80
Std	3.36	3.58	1.57	10.82	81.57	7.80	300.17	0.45	2.33	30.02	0.22
Min	4.40	18.70	6.80	22.00	398.90	24.70	244.00	1.59	0.00	116.10	0.55
Max	15.00	31.70	11.90	54.00	685.40	51.80	1040.00	2.99	6.00	221.00	1.21
Yuvarlak Stream mouth (YuvSM) (e)											
Mean	$4.57^{a,b,c,d}$	31.18^{a}	$8.98^{a,b,d}$	$47.62^{a,b}$	792.85^{c}	55.88^{c}	$1162.08^{b,c}$	3.37^{a}	$0.38^{a,c,d}$	$230.88^{a,c}$	$1.23^{a,b}$
Std	4.11	6.47	1.45	7.29	169.22	10.80	695.06	0.61	1.39	52.57	0.18
Min	0.00	19.40	6.60	32.00	560.10	41.80	524.00	2.42	0.00	152.00	0.88
Max	10.50	41.20	11.40	57.00	1209.70	78.60	2748.00	4.59	5.00	356.20	1.48
Sediment quality guidelines											
PEL		197.00	91.30	315.00	36.00					90.00	
ERM		390.00	110.00	270.00	50.00					145.00	
TEL		35.70	35.00	123.00	18.00					37.30	
ERL		70.00	35.00	120.00	30.00					80.00	

There is no statistical significance between the line and the superscript letters ($p < 0.05$)

Table 5 Sediment assessment methods results for the Kargıcak Stream region (KarSM) for the elements studied

	Cu	Pb	Zn	Ni	Cr	Co	Mn	Mo	Al (%)	Fe (%)
Contamination factor										
Mean	1.44	0.71	0.83	9.90	2.56	2.81	0.99	1.01	0.26	0.94
Min	0.92	0.57	0.67	0.35	1.09	1.60	0.77	0.00	0.21	0.68
Max	2.06	1.25	1.22	12.74	3.33	3.44	1.26	2.08	0.34	1.12
STD	0.34	0.20	0.15	3.34	0.81	0.65	0.16	0.74	0.04	0.15
Enrichment factor										
Mean	1.84	0.91	1.05	12.60	3.26	3.58	1.27	1.17	0.33	1.20
Min	1.18	0.72	0.86	3.84	1.39	2.04	0.98	0.00	0.27	0.86
Max	2.63	1.59	1.59	16.22	4.25	4.38	1.61	2.65	0.43	1.42
STD	0.44	0.25	0.19	4.25	1.04	0.83	0.20	0.92	0.06	0.19
Geoaccumulation index										
Mean	−0.09	−1.11	−0.88	2.60	0.68	0.86	−0.61	−0.74	−2.55	−0.69
Min	−0.70	−1.41	−1.15	1.01	−0.45	0.09	−0.97	−2.29	−2.85	−1.15
Max	0.46	−0.27	−0.30	3.09	1.15	1.20	−0.25	0.47	−2.14	−0.43
STD	0.35	0.33	0.24	0.70	0.58	0.39	0.23	1.10	0.24	0.24
Potential ecological risk factor										
Mean	7.21	3.57	0.83	49.48	5.12					
Min	4.62	2.83	0.67	15.08	2.19					
Max	10.31	6.23	1.22	63.68	6.67					
STD	1.72	0.99	0.15	16.68	1.63					
Toxic unit										
Mean	1.71	0.96	1.44	84.11	11.78					
Min	1.03	0.45	0.88	73.35	10.27					
Max	4.30	3.52	4.74	87.04	14.09					
STD	0.94	0.95	1.22	3.95	0.97					
			Degree of contamination			Modified degree of cont		Pollution load index		
Mean			21.45			2.15		1.13		
Min			12.22			1.22		0.00		
Max			26.12			2.61		1.43		
STD			4.94			0.49		0.43		
			Mean ERM quotient			Mean PEL quotient		Total toxic unit		
Mean			3.13			4.40		21.99		
Min			1.12			1.55		7.77		
Max			4.01			5.65		28.27		
STD			1.00			1.42		7.08		

Table 6 Sediment assessment method results for Namnam Stream region (NamSM) for the elements studied

	Cu	Pb	Zn	Ni	Cr	Co	Mn	Mo	Al (%)	Fe (%)
Contamination factor										
Mean	0.92	0.39	0.55	20.45	4.19	4.58	1.12	0.73	0.15	1.00
Min	0.73	0.34	0.45	0.35	3.18	3.49	0.81	0.00	0.12	0.73
Max	1.04	0.51	0.58	26.00	4.93	5.75	1.39	2.58	0.17	1.15
STD	0.08	0.05	0.04	3.75	0.59	0.77	0.17	0.79	0.02	0.13
Enrichment factor										
Mean	0.85	0.36	0.50	18.85	3.86	4.22	1.03	0.78	0.14	0.92
Min	0.67	0.31	0.42	13.59	2.93	3.22	0.75	0.00	0.11	0.68
Max	0.96	0.47	0.47	23.96	4.54	5.30	1.28	3.09	0.16	1.06
STD	0.07	0.05	0.03	3.45	0.54	0.71	0.16	0.92	0.02	0.12
Geoaccumulation index										
Mean	−0.71	−1.96	−1.46	3.75	1.47	1.59	−0.43	−1.45	−3.31	−0.60
Min	−1.04	−2.16	−1.73	3.30	1.08	1.22	−0.89	−2.96	−3.67	−1.03
Max	−0.53	−1.56	−1.37	4.12	1.72	1.94	−0.11	−0.29	−3.11	−0.38
STD	0.13	0.18	0.10	0.27	0.21	0.25	0.23	1.09	0.18	0.20
Potential ecological risk factor										
Mean	4.59	1.94	0.55	102.25	8.38					
Min	3.66	1.68	0.45	73.73	6.36					
Max	5.20	2.55	0.58	130.01	9.86					
STD	0.40	0.26	0.04	18.74	1.18					
Toxic unit										
Mean	0.50	0.21	0.39	89.17	9.74					
Min	0.38	0.14	0.30	88.03	8.97					
Max	0.63	0.34	0.48	90.20	10.78					
STD	0.08	0.06	0.06	0.74	0.61					

	Degree of contamination	Modified degree of cont	Pollution load index
Mean	34.09	3.41	0.98
Min	25.25	2.53	0.00
Max	40.88	4.09	1.35
STD	4.86	0.49	0.53

	Mean ERM quotient	Mean PEL quotient	Total toxic unit
Mean	6.16	8.66	43.28
Min	4.48	6.30	31.52
Max	7.75	10.89	54.45
STD	1.09	1.53	7.64

the values of Al and Zn in the lake sediment were compared with the Earth crust values, accumulation levels in the sediment were found to be very low. It is difficult to suggest an anthropogenic effect for these two elements because the EF value obtained based on the Earth crust reference is very low (Tables 5, 6, 7). This means that the strong relationship between these elements is of lithological origin. Similarly, it can be seen in the literature that Al and Zn demonstrate very strong correlations without exceeding the Earth crust values. Another interesting point between these two elements that draws our attention is that they are both concentrated in KarSM. In the sediment samples in this area, significantly higher levels of Al and Zn were detected compared to the lake in general and other important areas.

Copper was also evaluated. In particular, Cu content of the sediment samples near KarSM, which contain more Cu than the entire lake (Table 4), resulted in higher C_f^i values (Cu = 1.44) (Tables 5, 6, 7). According to the EF values (Cu = 1.84), an enrichment in Cu occurs. In addition, Igeo with a value of 2.60 is ranked at level 4 on the seven-level scale and indicates a moderate to strong contamination level. When we look at the elements that are most strongly

Table 7 Sediment assessment methods results for the entire Köyceğiz Lake for the elements studied

	Cu	Pb	Zn	Ni	Cr	Co	Mn	Mo	Al (%)	Fe (%)
Contamination factor										
Mean	0.75	0.46	0.49	10.46	2.35	2.56	0.84	2.45	0.14	0.65
Min	0.36	0.26	0.23	3.02	1.09	0.36	0.29	0.00	0.07	0.32
Max	2.06	1.25	1.22	26.00	4.93	5.75	3.23	5.77	0.34	1.15
STD	0.30	0.14	0.16	4.43	0.86	0.97	0.49	1.53	0.05	0.21
Enrichment factor										
Mean	1.16	0.75	0.77	16.08	3.63	3.93	1.27	3.85	0.22	1.00
Min	0.74	0.30	0.48	3.04	1.10	1.61	0.63	0.00	0.12	1.00
Max	1.85	1.27	1.23	22.63	4.47	5.09	4.07	9.07	0.34	1.00
STD	0.20	0.20	0.15	3.01	0.57	0.52	0.60	2.39	0.04	0.00
Geoaccumulation index										
Mean	−1.08	−1.75	−1.68	2.70	0.57	0.68	−1.04	0.68	−3.46	−1.27
Min	−2.06	−2.56	−2.70	1.01	−0.45	−0.33	−2.39	−3.56	−4.53	−2.24
Max	0.46	−0.27	−0.30	4.12	1.72	1.94	1.11	5.47	−2.14	−0.38
STD	0.47	0.35	0.43	0.53	0.47	0.49	0.74	1.42	0.46	0.44
Potential ecological risk factor										
Mean	2.31	0.49	52.31	4.70	4.70					
Min	1.80	1.28	0.23	15.08	2.19					
Max	10.31	6.23	1.22	130.01	9.86					
STD	1.47	0.67	0.16	22.13	1.71					
Toxic unit										
Mean	0.83	0.53	0.74	87.32	10.57					
Min	0.38	0.14	0.30	73.35	8.97					
Max	4.30	3.52	4.74	90.20	14.09					
STD	0.47	0.39	0.51	1.97	0.81					

	Degree of contamination	Modified degree of cont	Pollution load index
Mean	21.16	2.12	0.90
Min	12.01	1.20	0.00
Max	40.88	4.09	1.20
STD	6.02	0.60	0.31
	Mean ERM quotient	Mean PEL quotient	Total toxic unit
Mean	3.21	4.51	22.53
Min	1.12	1.55	7.77
Max	7.75	10.89	54.45
STD	1.31	1.85	9.23

correlated with Cu, it can be seen that these are Al and Zn, and Cu forms a strong correlation with these elements (Cu–Al = 0.88, Cu–Zn = 0.87) (Table 8). These correlations are also supported by CA (Table 9; Fig. 3). It can also be seen that these elements are introduced to the lake in significant amounts through the Kargıcak Stream. When we consider that the source of these two elements within the lake is natural based on sediment evaluation methods (Tables 5, 6, 7), and EF values in particular, the high concentration of Cu may not be anthropogenic despite its high EF values. It is known that EF gives high values when elements from natural sources produce high values in sediments (Lar and Gusikit 2015). Considering the relationships between these three elements derived from Kargıcak Stream inlet, a common natural source is more likely than a possible anthropogenic source.

Among our findings, perhaps the most important were the molybdenum results. Mo was not only the single element

Table 8 Correlation matrix of the studied elements

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cr	Al
Mo	1.000										
Cu	−0.409	1.000									
Pb	−0.258	0.539	1.000								
Zn	−0.561	0.874	0.623	1.000							
Ni	−0.446	0.614	0.063	0.511	1.000						
Co	−0.571	0.724	0.246	0.680	0.934	1.000					
Mn	−0.823	0.543	0.371	0.706	0.596	0.743	1.000				
Fe	−0.682	0.863	0.418	0.855	0.821	0.889	0.798	1.000			
As	−0.490	0.434	−0.029	0.387	0.477	0.520	0.472	0.532	1.000		
Cr	−0.493	0.619	0.092	0.524	0.965	0.907	0.638	0.811	0.506	1.000	
Al	−0.537	0.880	0.667	0.943	0.515	0.670	0.699	0.859	0.273	0.518	1.000

with significant negative correlation among all studied elements, but also showed negative correlation with all other elements (Table 8). CA results also fully support this situation. In the dendrogram, Mo is also clearly separated in a different cluster from all other elements (Fig. 3). In the proximity matrix, its distance to other elements ranges from 14.37 to 16.73 Euclidian distances. These values are the largest for distance among all the elements (Table 9). This means that the source of Mo's accumulation in the lake is different from the source of other elements. However, EF values indicate Mo enrichment in the lake. Interpolation maps for Mo (Fig. 2h) show that the area with the highest density in the lake is the in-lake water source located south of the lake. Statistically, this area contains significantly more Mo than the areas NamSM and KarSM (Table 4). Despite the fact that it contains more Mo than the area near Yuvarlak Stream and the lake in general, this difference is not statistically significant. Groundwater sources can carry large quantities of Mo (Wang et al. 2016; Jones 2017). Based on these findings, it is clear that the factor constituting a significant proportion of Mo in lake sediments is a groundwater source located to the south.

Based on our findings, Pb, As, Mn and Fe do not pose an environmental risk. These elements are within the limit values for all values analyzed, and do not behave differently across the lake.

Environmental impact of the current element levels in the lake

The effect of current element concentrations in the lake on living organisms was investigated near stream inlets, water inflows and the entire lake using different methods. According to the sediment quality guidelines, there are two elements that could pose a threat to the lake. These are Ni and Cr. Both elements have values above all criteria (Table 4). Although Ni is an essential micronutrient for the metabolism of some aquatic organisms, it is also

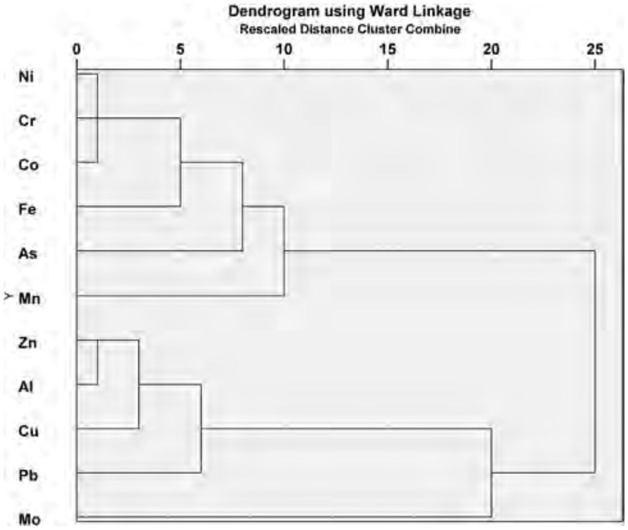

Fig. 3 Cluster analysis (CA) dendrogram showing the relationships between the elements studied in the sediments of Köyceğiz Lake

toxic in high concentrations (Bielmyer et al. 2013). Moreover, it is also not clear whether Ni is essential for animals (Blewett and Leonard 2017). Rocks, volcanic activity and forest fires are natural sources of Ni, coal and oil fumes, wastewater, electroplating, cement and steel industry activity, and phosphate-containing fertilizers all contain Ni (Savorelli et al. 2017). The toxic characteristics of Ni emerge in five different ways: (1) disruption of Ca^{2+} homeostasis, (2) disruption of $Fe^{2+/3+}$ homeostasis, (3) ROS-induced oxidative damage, (4) disruption of Mg^{2+} homeostasis and (5) allergic response of respiratory epithelia. These pathways manifest themselves in three different ways: (1) reducing the availability of Ca^{2+} required for exoskeleton, shell and bone formation, (2) respiratory disturbance and (3) cytotoxicity and tumor formation (Brix et al. 2017). Cr is found naturally in rocks, soil and volcanic emissions; anthropogenic sources of Ni include

Table 9 Proximity matrix of the cluster analysis performed on the studied elements

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cr	Al
Mo	0.00										
Cu	15.27	0.00									
Pb	14.37	7.79	0.00								
Zn	15.69	4.70	5.57	0.00							
Ni	15.46	10.30	13.94	11.25	0.00						
Co	16.04	9.16	12.81	9.83	2.33	0.00					
Mn	16.73	11.15	11.61	10.15	9.65	8.67	0.00				
Fe	16.49	5.64	10.11	6.32	5.98	4.55	8.64	0.00			
As	15.49	9.90	11.66	9.93	7.51	7.29	10.82	7.73	0.00		
Cr	15.84	9.24	13.38	10.45	2.10	2.43	9.11	4.98	7.36	0.00	
Al	15.63	3.64	5.90	2.47	11.42	10.01	10.15	6.29	10.64	10.47	0.00

alloys and coatings, stainless steel production in the automotive sector, nuclear and high-temperature research, and paint and metallurgical industries (Vaiopoulou and Gikas 2012). Despite its role in carbohydrate metabolism as part of the glucose tolerance factor, it is associated with cardiovascular risks and some metabolic syndromes (Bilandžić et al. 2017). The presence of a toxic effect or the nature of the toxic effect depends on the concentration and valence. Although its valence can vary between − 2 and + 6, it is mostly found in nature in its most stable forms of + 3 and + 6 valence. Of these forms, + 6 is more toxic and is the non-essential form with higher dissolution properties (Ergul-Ulger et al. 2014).

Toxic unit results indicate that Ni has the highest environmental risk factor for the lake (Tables 5, 6, 7). Ni alone makes up 87% of the total toxic effect in the lake. This rate is 84% in KarSM and 89% in NamSM. According to the total toxic unit values, the area where the toxic effect is most apparent is NamSM, with a value of 43, and the area with the lowest toxic effect is HotSR with a value of 17. The mean effect range-median quotient (m-ERM-q) and mean probable effect level quotient (m-PEL-q) values were used separately on lake sediments for different regions, to understand the toxic effect rate of element accumulation on living organisms. These results also support total toxic unit results. According to m-ERM-q and m-PEL-Q values, the area with the highest toxic effect on living organisms is NamSM, and the area with the least toxic effect is HotSM. However, all m-ERM-q and m-PEL-Q values in terms of both the regional analysis and for the entire lake show toxic effects at the top of their scales. The rate of impact according to m-ERM-q is over 76%. According to m-PEL-q values, all regions are at a “highly impacted” level.

Although Cd was also studied in the lake, it was at concentrations below the limits of detection, and therefore they were not included in the tables. The findings of previous studies at different locations can also be seen in Table 10.

Conclusion

The sediment element accumulation levels, relationships between the accumulated elements and the effects on the ecosystem have been investigated in Köyceğiz Lake, both in sub-regions and across the entire lake. Multivariate statistical techniques, sediment assessment methods and interpolation maps were effective tools in understanding the contamination in the lake.

The results show that the highest level of element is found in the sediment samples taken from the area near Namnam and Kargıcak stream inlets, and the lowest element concentrations were found in the area where there are in-lake groundwater sources. According to sediment assessment methods, these two regions have the highest contamination level and the degree of contamination in these regions varies between the upper–intermediate and the highest levels, while showing some differences based on the methods used. Average lake element concentrations are low compared to other inlet areas, although the lake sediments still show element contaminations. The sources of the high contamination values observed in the lake were determined to be primarily Ni and to some extent Cr. These two elements, particularly in the area where Namnam Stream flows into the lake, are above the limit values for the lake, and this creates contamination throughout the lake. Ni and Cr were found to be highly statistically correlated. Apart from these two elements, there is no significant element contamination in the lake. When the effect of existing element accumulation on the ecosystem was evaluated, the two different methods used gave the highest toxic effect values.

Based on these findings, we can conclude that in-depth studies should be carried out in the lake for Ni and Cr, but

Table 10 Comparison of metal accumulation indices in the sediments of Köyceğiz Lake with previous studies

		Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cr	Al	
Abu Khashaba coastline, Egypt	Cf	NA	0.52	18.80	1.84	6.69	3.62	0.64	2.22	22.59	0.00	NA	El sorogy et al. (2016)
	EF	NA	0.26	10.60	0.79	3.16	1.93	0.36	NA	12.64	0.00	NA	
	Igeo	NA	−1.61	3.23	0.72	2.11	1.27	−1.21	0.41	3.91	−5.96	NA	
Koumoundourou Lake, Greece	Igeo	NA	2.58	0.61	2.68	−0.20	NA	NA	NA	1.69	3.56	NA	Hahladakis et al. (2013)
North-western part of Elefsis Bay, Greece	Igeo	NA	−0.22	0.61	1.29	−0.52	NA	NA	NA	1.14	2.16	NA	
Outer part of İzmir Bay, Turkey	EF	NA	0.51	NA	1.35	1.24	NA	0.58	1.15	NA	NA	NA	Kontas (2008)
Inner part of İzmir Bay, Turkey	EF	NA	0.93	NA	2.55	1.36	NA	0.54	1.2	NA	NA	NA	
Thermaikos Gulf, Greece	EF	NA	2.9	5.1	1.7	NA	NA	NA	NA	NA	NA	NA	Christophoridis et al. (2009)
Homa Lagoon, Turkey	Cd	7.07 (Average value)											Uluturhan et al. (2011)
	Cf	NA	0.41	0.53	0.75	1.25	NA	0.66	0.5	NA	1.14	0.32	
Edku Lake, Eygpt	PLI	4.6											El-Said et al. (2014)
	RI	68.8											
	Cd	48											
	mCd	6.9											
Candarli Gulf, Turkey	Cd	11.68 (average value)											Pazi (2011)
	Cf	NA	1.06	1.37	1.52	0.89	NA	1.49	NA	1.12	0.99	NA	
Langat River, Malaysia	EF	NA	1.94	9.45	5.95	NA	NA	NA	NA	80.53	NA	NA	Shafie et al. (2012)
	Igeo	NA	−1.48	0.23	−0.2	NA	NA	NA	NA	2.24	NA	NA	
Köyceğiz Lake, Turkey	Cf	0.78	1.45	1.13	1	1.24	1.3	1.11	1.23	NA	1.24	1.27	Current study (average value)
	EF	0.65	1.18	0.97	0.83	1.01	1.06	0.89	1	NA	1.01	1.04	
	Igeo	1.94	−0.13	−0.46	−0.65	−0.38	−0.29	−0.63	−0.36	NA	−0.36	−0.32	
	Cd	11.74											
	mCd	1.17											
	PLI	0.93											

most importantly Ni. In these studies, it is of utmost importance that the source of these elements be clearly determined, and the status of accumulation in living organisms, especially those living in the sediments, be revealed.

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