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AN EXAMINATION OF ECOLOGICAL AND STATISTICAL RISK ASSESSMENT OF TOXIC METALS IN SEDIMENTS AT SIDDIKLI DAM LAKE: A CASE STUDY IN KIRSEHIR, TURKEY

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ABSTRACT

This study was carried out in order to examine heavy metals concentration in sediment of Sıddıklı Dam Lake in Kırşehir, Turkey. The surface sediment samples from four stations in the Sıddıklı Dam Lake were collected seasonally from September 2015 to August 2016. Concentrations of selected metals were determined using ICP-MS.

Descriptive statistical analysis including One-way ANOVA, significance (0.05) was done. Important differences in the mean values were tested using Tukey's multiple range test. Moreover, Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) were applied to the data of the dam lake.

The degree of metal contamination is compared with the standard shale values. The result of sediment enrichment factor, pollution loading index, and geoaccumulation index reveals that the surface sediments of the dam lake are not polluted.

Thus, this study aims to identify the main pollution factors as well as the regions of the lake that are at risk. Moreover, significant correlations between the measured concentrations of the all heavy metals in the sediment samples were observed. It can be concluded that the heavy metal pollution level is low at Sıddıklı Dam Lake, however it will be good to adopt protective measures before it is too late.

KEYWORDS:
Heavy Metal, Accumulation, Sediment, Multivariate Statistical Methods

INTRODUCTION

Sediment pollution with heavy metals has become a serious health concern over recent years. These metals are common pollutants that have distributed aquatic environments. Heavy metals in sediments are derived from natural components or geological as well as from anthropogenic sources. Today, the most common metal pollutants are arsenic, mercury, cadmium, lead, chromium, copper, and nickel. Although some metals such as manganese, copper, and zinc are essential trace elements for organisms, they can also be dangerous at high exposure levels [1].

The sources of metals in aquatic sediments are either natural or anthropogenic [2]. The natural sediments may extensively be contaminated with various heavy metals released from domestic wastewater and/or industrial effluents, the dumping of agricultural activity, and other types of anthropogenic activities [3-5]. Heavy metals in sediments are bioaccumulated by organisms either passively from the water or by facilitated uptake. Moreover, heavy metals that are consumed by organisms may enter the food chain in significant amounts. Also, sediments play a critical major role in determining the pollution pattern of freshwater systems. They are responsible for transporting a significant proportion of many nutrients and toxic chemicals. Many studies reported that these resources within Turkey have been seriously polluted by heavy metals [6-14].

The city of Kırşehir is rich in freshwater resources, being endowed with a network of rivers that can meet a variety of the region's water needs. However, with the rapid increase in the population of the city and the need to meet the increasing demands of irrigation consumption mean that the available water resources are becoming depleted, and that the water quality has deteriorated. The Sıddıklı Dam Lake is very vital to Kırşehir as it provides very wide area of irrigation water.

FIGURE 1
Study area with sampling point locations (adapted from Google earth)

The aim of the present study was:

1. To determine the level of heavy metal concentration,
2. To determine the ecological risk in surface sediments of Sıddıklı Dam Lake, and
3. To assess sediment quality.

In addition, all results collected from this study will provide the baseline information for future studies.

MATERIALS AND METHODS

Sample location and sampling. The surface sediment samples were collected seasonally between September 2015 and August 2016 from 4 stations. Surface sediment samples (0-20 cm) were collected in triplicates and homogenized in a zip locked polyethylene bag at each sampling site using an Ekman sampler. Afterwards, the collection the samples were placed in coolers with ice bags while being transported to the laboratory, whereby they were kept at about -80°C until being analyzed.

Heavy metal analysis. The samples were immediately transported to the laboratory and filtered through acid treated Millipore HA filters (0.45 µm) using a vacuum. These samples were stored in darkness at 4 °C up until analysis [15]. Sediment samples were prepared with a preliminary digesting process via a CEM MARS-5 model microwave instrument. Heavy metal determinations of all of the samples were carried out using an ICP-MS -Bruker 820-MS [16]. The reference materials were used to check the accuracy and reliability of the method. Metal contents were expressed in terms of µg/g.

Enrichment factor, Pollution Loading Index and Index of Geoaccumulation. The enrichment factor (EF) and Geoaccumulation index (I_{geo}) are some useful indicators for reflecting the status of environmental contamination [17-20]. In calculating the normalized enrichment factors (EF), the original Salomons and Förstner [21] equation was substituted in the present study with Fe. In order to evaluate a possible anthropogenic origin of the metals, the enrichment factor (EF), pollution loading index (PLI), and I_{geo} were calculated for the metal concentration obtained in the surface sediments [22].

Statistical Analysis. Statistical analysis of data was carried out using SPSS statistical package programs. Descriptive statistical analysis including One-way ANOVA was done, with a significance of 0.01 and 0.05. Important differences in the mean values were tested using Tukey's multiple range test. Moreover, relationships among the considered variables were tested using Pearson's correlation. Multivariate analyses of the dam lake data set were performed using Principal component analyses (PCA) and cluster analysis (CA). All of the statistical calculations were performed using SPSS 17.0.

RESULTS AND DISCUSSION

Heavy metal analyses of sediment samples taken periodically from four stations over a period of 4 seasons had showed that the mean levels of aluminium (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), barium (Ba) and lead (Pb) varied had between 214.248-3204.650 (2246.891±178.055), 7.713-12.584 (9.686±0.311), 3.532-6.030 (4.723±0.184), 81.446-149.488 (113.

324±4.692), 3229.803-5451.602 (4637.034±137.871), 0.695-1.692 (1.271±0.073), 1.988-5.614 (3.250±0.313), 0.157-2.091 (0.970±0.157), 4.000-11.944 (7.194±0.452), 0.142-0.896 (0.580±0.052), 33.767-85.124 (47.231±2.900), and 4.145-8.122 (5.595±0.255), µg/g, respectively. Moreover, seasonal changes of heavy metal concentrations in the surface sediment are shown in Table 1. The sequence of the means of heavy metals in water samples from each season were Fe>Al>Mn>Ba>V>Zn>Pb>Cr>Ni>Co>Cu>Ga. Also, the concentration of other elements -that is, light metals such as Ca, Na, and K- and total phosphorous varied between as a µg/g 7246.048-37642.340 (19736.146±2657.994), 5-10.4 (7.639±0.454), 4.4-7 (5.663±0.190) and 0.387-0.676 (0.507±0.021). Calcium was identified as being the most abundant element. Also, other sediment parameters such as water content and organic matter as a percentage 10.650-17.7(13.352±0.612), 2.240-4.560 (2.837±0.151) were determined. The pH of the sediment had varied from 6.4 to 7.4. The average concentrations of the majority all metals in the sediment were lower than the average shale values. Also, the average concentrations of Cr, Mn, Co, Ni, Cu, Zn and Pb obtained in this study were much lower than sediments of other studies (Table 2). Moreover, in the present study, the metal concentrations in the dam lake sediments are compared with TEC and PEC values. The means of Cr, Ni, Cu, Zn and Pb in our samples were lower than TEC and PEC values (Table 2).

TABLE 1
Seasonal changes in Levels of Heavy Metals

Season		Al (µg/g)	Ca (µg/g)	V (µg/g)	Cr (µg/g)	Mn (µg/g)	Fe (µg/g)	Co (µg/g)	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)
Fall	Mean	1704.631	10925.378^{a}	9.216	4.616^{a}	91.938^{a}	4590.873	1.045^{a}	2.440^{a}	0.600^{a}	7.505
	SE±	513.165	748.400	0.595	0.381	3.795	195.585	0.058	0.249	0.204	1.561
	Min.	214.248	8805.082	7.880	3.532	81.446	4074.272	0.974	2.112	0.157	4.645
	Max.	2405.810	12210.750	10.766	5.270	99.408	4954.949	1.219	3.168	1.147	11.944
Winter	Mean	2854.968	11380.594^{a}	9.447	4.223^{a}	118.442^{ab}	4817.414	1.255^{a}	2.393^{a}	0.548^{a}	7.235
	SE±	148.753	1680.431	0.107	0.014	5.418	143.544	0.026	0.164	0.023	0.473
	Min.	2478.738	7246.048	9.186	4.199	105.540	4474.711	1.187	1.988	0.493	6.071
	Max.	3204.650	15478.280	9.708	4.257	131.748	5177.031	1.306	2.789	0.606	8.389
Spring	Mean	1888.362	20921.106^{b}	9.219	4.308^{a}	111.430^{ab}	4323.053	1.121^{a}	2.916^{a}	0.767^{a}	6.177
	SE±	215.883	1564.667	0.644	0.107	8.148	446.078	0.161	0.138	0.032	0.880
	Min.	1319.820	16981.110	7.713	4.016	92.044	3229.803	0.695	2.692	0.689	4.000
	Max.	2281.935	24639.220	10.841	4.488	131.834	5415.124	1.386	3.260	0.834	8.312
Summer	Mean	2539.606	35717.505^{c}	10.862	5.745^{b}	131.487^{b}	4816.796	1.662^{b}	5.252^{b}	1.964^{b}	7.858
	SE±	96.546	845.878	0.726	0.175	7.608	259.102	0.018	0.145	0.049	0.361
	Min.	2303.057	33518.830	9.032	5.255	112.879	4182.268	1.612	4.908	1.853	6.963
	Max.	2776.026	37642.340	12.584	6.030	149.488	5451.602	1.692	5.614	2.091	8.730
Total	Mean	2246.891	19736.146	9.686	4.723	113.324	4637.034	1.271	3.250	0.970	7.194
	SE±	178.055	2657.994	0.311	0.184	4.692	137.871	0.073	0.313	0.157	0.452
	Min.	214.248	7246.048	7.713	3.532	81.446	3229.803	0.695	1.988	0.157	4.000
	Max.	3204.650	37642.340	12.584	6.030	149.488	5451.602	1.692	5.614	2.091	11.944

Season		Ga (µg/g)	Ba (µg/g)	Pb (µg/g)	Na (µg/g)	K (µg/g)	TP (µg/g)	pH	WC (%)	OM (%)
Fall	Mean	0.463^{ab}	55.277	6.982^{b}	9.175	6.275	0.515	6.825	14.998^{b}	3.495
	SE±	0.058	10.838	0.406	1.126	0.335	0.060	0.144	1.462	0.477
	Min.	0.319	33.767	6.284	5.800	5.400	0.387	6.400	11.070	2.260
	Max.	0.559	85.124	8.122	10.400	7.000	0.676	7.000	17.700	4.560
Winter	Mean	0.768^{b}	39.433	5.210^{a}	6.125	5.075	0.542	7.155	11.008^{a}	2.500
	SE±	0.036	0.160	0.099	0.390	0.138	0.010	0.022	0.124	0.103
	Min.	0.680	39.058	4.956	5.000	4.800	0.511	7.100	10.650	2.240
	Max.	0.857	39.838	5.438	6.800	5.400	0.553	7.200	11.210	2.740
Spring	Mean	0.405^{a}	49.656	5.120^{a}	8.325	5.900	0.542	7.125	12.273^{ab}	2.713
	SE±	0.102	1.914	0.396	0.905	0.557	0.044	0.094	0.472	0.126
	Min.	0.142	44.570	4.145	6.400	4.400	0.429	7.000	10.960	2.350
	Max.	0.642	53.859	6.085	10.400	7.000	0.635	7.400	13.090	2.920
Summer	Mean	0.684^{ab}	44.559	5.069^{a}	6.933	5.400	0.429	6.948	15.130^{b}	2.640
	SE±	0.095	0.893	0.334	0.092	0.041	0.000	0.050	0.963	0.051
	Min.	0.479	42.357	4.325	6.800	5.300	0.428	6.800	13.230	2.560
	Max.	0.896	46.659	5.861	7.200	5.500	0.430	7.010	17.670	2.790
Total	Mean	0.580	47.231	5.595	7.639	5.663	0.507	7.013	13.352	2.837
	SE±	0.052	2.900	0.255	0.454	0.190	0.021	0.053	0.612	0.151
	Min.	0.142	33.767	4.145	5.000	4.400	0.387	6.400	10.650	2.240
	Max.	0.896	85.124	8.122	10.400	7.000	0.676	7.400	17.700	4.560

Horizontally, letters a, b and c show statistically significant differences in same group of metals ($p < 0.05$).

TABLE 2
Comparison of heavy metals in the previous studies

		Metals (µg/g)											
		Al	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ba**	**Pb**
This study		2246.891	9.686	4.723	113.324	4637.034	1.271	3.250	0.970	7.194	0.580	47.231	5.595
Seyhan Dam Lake [10]				118.95	803.63	39.350			19.80	39.09			
Kapulukaya Dam Lake [23]		%3.39		426.84	601.97	%2.48	24.19	71.71	17.66	51.86			21.16
Gala Lake [24]				67.42				34.20	12.52	50.46			11.71
US EPA				26				16	16	110			31
Shale Value [25]		80.000	130	90	850	47.200	19	68	45	95	19	580	
Threshold Effect Concentrations [26]	TEL			37.3				18	35.7	123			35
	LEL			26				16	16	120			31
	MET			55				35	28	150			42
	ERL			80				30	70	120			35
Probable Effect Concentrations [26]	PEL			90				36	197	315			91.3
	SEL			110				75	110	820			250
	TET			100				61	86	540			170
	ERM			145				50	390	270			110

TEL Threshold effect level, LEL lowest effect level, MET minimal effect threshold, ERL effect range low, PEL probable effect level, SEL severe effect level, TET toxic effect threshold, ERM effect range median.

The influences of anthropogenic metals pollution in surface sediments of Sıddıklı Dam Lake were determined using enrichment factor (EF-PLI) and geoaccumulation index (I_{geo}) for each of the metals (Table 3). The I_{geo} had suggested that individual metal contamination in the sediments could be classified as being "practically uncontaminated". The mean result from the present investigation had showed that I_{geo} of Cu: -6.3, V: -4.3, Cr: -4.8, Mn: -3.5, Co: -4.5, Ni: -5.1, Zn: -4.3, Ga: -5.7, Ba: -4.2, Pb: -2.4, Al: 7.5, Ca: 9, and Fe: 9.4, respectively. Contamination factor (EF) is a useful indicator reflecting the status of environmental contamination. The results from this study show that enrichment factors of all metals had varied from 0 to 1, and were classified as having "no enrichment". Also, the PLI index provide a simple, comparative means for assessing the level of metal pollution. The result from present study are classified as having no metal pollution except for Fe, Ca, and Al which are known as being the most common elements within Earth's crust. According to Varol [27], PLI values between 1.02 and 4.19 (mean 1.88) indicate that the Tigris River is moderately polluted. Also, the mean EF values for all metals (Cr and Mn except) were higher than 1.5, which suggests an anthropogenic impact on the heavy metal levels in the sediment of the Tigris River. Kankılıç et al. [23] had found evidence of heavy metal pollution in the Kapulukaya Dam Lake (Kırıkkale), with EF values that were over the pollution limits. Çevik et al. [10] had investigated the accumulation of heavy metals in the surface sediment of the Seyhan Dam Lake in Adana, Turkey. Their data were assessed using the I_{geo}, and had indicated that the surface sediment samples were partially contaminated with Cd which is used in agricultural activities as a fertilizer and pesticides.

TABLE 3
SEF, PLI and Igeo values in surface sediments

	Igeo	EF	PLI
Cu	-6.3	0.0	0.02
Al	**7.5**	0.3	274.75
Ca	**9.0**	0.9	793.59
V	-4.3	0.0	0.07
Cr	-4.8	0.0	0.05
Mn	-3.5	0.0	0.13
Fe	**9.4**	1.0	985.64
Co	-4.5	0.0	0.07
Ni	-5.1	0.0	0.05
Zn	-4.3	0.0	0.08
Ga	-5.7	0.0	0.03
Ba	-4.2	0.0	0.08
Pb	-2.4	0.0	0.28

According to statistical analysis (One-Way ANOVA) Ca, Cr, Mn, Ni, Co, Cu, Ga, Pb and WC in sediment concentrations were significantly different between the seasonal changes ($p<0.05$). Furthermore, Table 3 shows the statistical analysis of correlation matrix in terms of linear correlation coefficient (r) values (significant at 0.05 and 0.01) in sediment samples across all seasons, respectively. A positive correlation exists between V, Cr, Al and Ca, Mn, Cr, Ca, and V, Mn, Fe, V, and Cr, Fe, Co, Cr, and Mn, Ni, Cu, Fe, and Co, Cu, Zn, Co, and Ni, Zn, Ga, Ni, and Cu, Ga, Ba, Cu, and Zn, Na, K, Ba, and Pb. Also, a negative correlation exists between TP, pH, Na, and K (Table 4). A large portion of the results from this study correlate with those of other studies [28, 30].

Four principal components (PC) were obtained with an eigenvalue of more than 1, explaining greater than 85.35 % of total variance. PC 1 grouped metals such as Cr, Ni, cu, Ca, Co reveal 39.61 % of the total variance. Cr, Cu and Ca had originated from natural sources [31]. Cr and Ni are derived from terrigenous detritus material [32]. Also, PC 2 explains 24.22 % of the total variance and reveals high loading values for the Al, V, Ga, Co, Zn, TP, Mn and Fe, which are predominantly contributed by the agricultural runoff [30]. A similar result was shown in sediment samples taken from Iznik Lake [33]. PC3 (13.16 % of total variance) is the strong loading of Ba, Pb, Na, and K with WC and OM, confirming that metals from organic complexes exist within the sediment structure [34]. The fourth PC was explaining 8.18 % of the total variance has strong positive loadings on Ba, moderate positive loadings on pH, and weak negative loadings on Pb. Thus, this indicates pollutants from the metal group, which indicates some source of stream runoff (Table 5, Figure 2).

The present study Hierarchical cluster analysis (HCA) was used to show sampling stations with similar characteristics in the dam lake reservoir. The first cluster corresponds to station 1. This station is situated at the deepest and closest part to the door area of the dam lake. Also, Cluster 2 corresponds to 4 and 2, 3. These stations are situated very close to the river discharge sampling location. These zones mostly receive their pollution from agricultural runoff activities and soil erosion (Figure 3).

TABLE 4
Pearson correlation coefficients between heavy metal levels in Sıddıklı Dam Lake

	Al	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Al	1									
Ca	0.150	1								
V	**0.573***	**0.607***	1							
Cr	**0.185**	**0.751****	**0.590***	1						
Mn	0.524*	**0.700****	**0.757****	**0.497***	1					
Fe	0.467	0.239	**0.778****	**0.357**	**0.690****	1				
Co	0.512*	0.785**	0.779**	**0.656****	**0.809****	**0.600***	1			
Ni	0.201	**0.939****	0.508*	0.811**	**0.612***	**0.199**	**0.769****	1		
Cu	0.248	**0.907****	0.592*	0.892**	0.562*	**0.216**	**0.800****	**0.921****	1	
Zn	0.373	0.229	0.705**	0.530*	0.424	0.763**	**0.523***	**0.181**	**0.392**	1
Ga	0.727**	0.169	0.559*	0.365	0.647**	0.695**	0.612*	**0.227**	**0.278**	**0.490**
Ba	-0.261	-0.074	0.067	0.274	-0.309	-0.017	-0.166	-0.164	**0.130**	**0.542***
Pb	-0.243	-0.371	0.012	0.006	-0.284	0.344	-0.264	-0.269	-0.350	0.197
Na	-0.377	-0.100	0.010	0.151	-0.235	0.203	-0.123	-0.134	-0.045	0.315
K	-0.246	-0.066	0.108	0.066	-0.130	0.346	-0.010	-0.086	-0.090	0.264
TP	-0.220	-0.591*	-0.655**	-0.817**	-0.543*	-0.652**	-0.685**	-0.588*	-0.725**	-0.816**
pH	0.097	-0.061	-0.103	-0.037	0.228	-0.062	-0.117	-0.165	-0.047	0.021
WC	-0.091	0.352	0.234	0.689**	-0.061	0.167	0.329	0.472	0.578*	0.505*
OM	-0.359	-0.280	-0.280	0.206	-0.458	-0.091	-0.374	-0.135	-0.112	0.067

	Ga	Ba	Pb	Na	K	TP	pH	WC	OM
Al									
Ca									
V									
Cr									
Mn									
Fe									
Co									
Ni									
Cu									
Zn									
Ga	1								
Ba	-0.281	1							
Pb	0.011	0.152	1						
Na	-0.149	**0.587***	**0.595***	1					
K	-0.064	**0.324**	**0.681****	0.915**	1				
TP	-0.452	-0.412	-0.083	**-0.389**	**-0.340**	1			
pH	0.130	0.185	-0.477	**-0.049**	**-0.287**	-0.015	1		
WC	-0.022	0.568*	0.319	0.602*	0.516*	-0.704**	-0.290	1	
OM	-0.221	0.492	0.634**	0.693**	0.564*	-0.143	0.018	0.592*	1

$^{**}p < 0.01$
$^{*}p < 0.05$

TABLE 5
Varimax rotated factor matrix for the whole data set

Variable	PC 1	PC 2	PC 3	PC 4
Eigenvalues	7.525	4.602	2.501	1.589
% of Variance	39.61	24.22	13.16	8.36
Accumulative %	39.61	63.82	76.99	85.35
	Factor loadings (varimax normalized)			
Al	0.069	**0.724**	-0.338	0.081
Ca	**0.933**	0.159	-0.158	-0.050
V	0.473	**0.770**	0.044	-0.049
Cr	**0.850**	0.262	0.274	0.095
Mn	0.483	**0.715**	-0.313	0.040
Fe	0.097	**0.920**	0.240	-0.145
Co	**0.717**	**0.606**	-0.145	-0.106
Ni	**0.953**	0.117	-0.127	-0.161
Cu	**0.970**	0.178	-0.007	0.101
Zn	0.255	**0.708**	0.472	0.265
Ga	0.090	**0.856**	-0.138	0.004
Ba	0.095	-0.114	**0.717**	**0.562**
Pb	-0.318	0.125	**0.706**	**-0.524**
Na	-0.027	-0.019	**0.916**	-0.023
K	-0.060	0.112	**0.814**	-0.338
TP	**-0.645**	**-0.518**	-0.464	-0.166
pH	-0.131	0.082	-0.156	**0.849**
WC	**0.589**	-0.029	**0.734**	-0.031
OM	-0.073	-0.272	**0.805**	0.034

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 5 iterations.

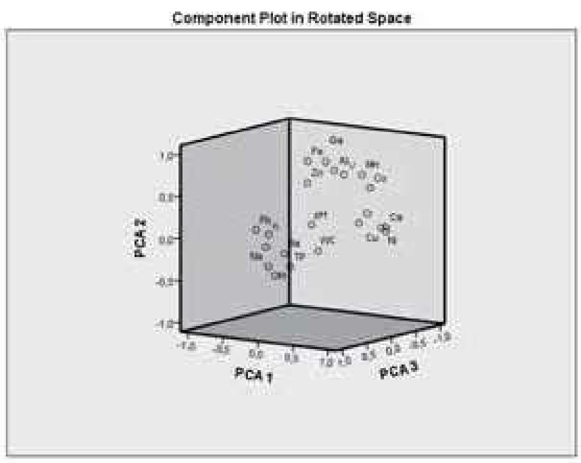

FIGURE 2
Component plot

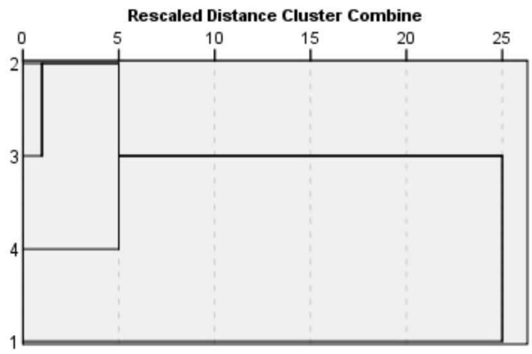

FIGURE 3
Dendogram (using Ward Method) shows clusters of variables

CONCLUSIONS

The present results indicate that heavy metal contamination in the surface sediment of Sıddıklı Dam Lake is lower than reference values. Seasonal variation of metals from sediment are statistically significant. Moreover, a positive relationship was found between metals. The study revealed that on the basis of computed indexes (EF, PLI and I_{geo}) Sıddıklı Dam Lake is classified as being unpolluted. In total, all four of the PCA accounts for 85.35 % of the total variance demonstrated, and that the lithogenic factor dominates the distribution of most of the metals. Furthermore, it is probable that these elements had originated from agricultural activities around the lake. Consequently, given the current situation, the lake needs to be protected through a protection and regular monitoring program.

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