Ecological Indicators 119 (2020) 106784

Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind

Geographical information systems based ecological risk analysis of metal accumulation in sediments of İkizcetepeler Dam Lake (Turkey)☆

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ARTICLE INFO

Keywords:
Metal pollution
Environmental degradation
Aquatic ecosystems
Pollution dynamics
Ecological risk

ABSTRACT

This study analyzed the spatial distribution, potential ecological risks and possible sources of metal concentrations, organic carbon, chlorophyll degradation products and $CaCO_3$ content from surface sediment samples in İkizcetepeler Dam Lake using ecological-toxicological indices, multivariate statistical analysis, and geographical information systems (GIS) software. One core sample and 32 surface sediments were taken from the Dam Lake, while seven lithologic samples were taken from various points in the basin. To identify anthropogenic influences in the Dam Lake from the before dam was constructed period to the present day, the enrichment factor (EF), contamination factor (CF), geoaccumulation index (I_{geo}), toxic risk index (TRI) and pollution load index (PLI) indices were calculated based on lithologic background values. Modified ecological risk (mER) and modified potential ecological risk (mPER) were calculated separately according to core sample and lithologic background values. Therefore, ecological risk during Anthropocene was determined using core sample values. Results pointed to significant enrichment of Ni (6.93), moderate enrichment of As (3.88), Cr (2.86), Mn (2.54), Hg (2.34), and Cd (2.04) and low level enrichment of Pb (1.20), Cu (1.15), Zn (1.08), and Fe (0.80). Ecological risk was listed as Hg (94) > Cd (61) > As (38) > Ni (35) > Cu (5.98) > Cr (5.72) > Pb (5.68) > Zn (1.07) according to lithologic background values and as Hg (59) > Cd (29) > As (9) > Ni (8) > Cu (7) > Pb (5) > Cr (2.97) > Zn (1.42) according to core background values. A significant level of ecological risk was determined for Hg (94), medium level ecological risk for Cd (61), and close to moderate level ecological risk for As (38) and Ni (35). The risk was low for all the other metals. According to the core sample background values, ecological risk was at the lowest limit of the most significant level for Hg (81), moderate for Cd (50) and low for other metals. Overall, this indicates a low (123) and moderate (201) potential ecological risk in İkizcetepeler Dam Lake based on core and lithologic background values, respectively.

1. Introduction

Metals are natural components of the earth's crust and important elements in the metabolism of biota (e.g., Cu, Zn and Fe). However, some metals create ecological risks due to their domestic use and industrial production (Uwah et al., 2013; Tagliaferro, et al., 2018) Ecological risk analysis is one of the best methods to detect the potential issue of metal pollution and its impacts on ecosystem, in particular on wetlands. Ecological risk analyses can be easily incorporated in decision-making processes for detecting environmental issues and managing ecosystem health. The transportation of metals to aquatic ecosystems may occur from either natural factors such as lithologic structure or anthropogenic disturbances. One of the most important goal when conducting ecological risk studies in lake sediments is to distinguish the natural and anthropogenic sources of metals and to determine the extent of the ecological risk.

Ecological risk indices provide robust and reliable result such as enrichment factor (EF), contamination factor (CF), ecological risk factor (mER), geoaccumulation index (I_{geo}), potential ecological risk (mPER), and pollution load index (PLI). EF, CF, and I_{geo} test the presence of anthropogenic effects, while the toxic effects and risk assessment of metals are determined with the TRI, mER, mPER, and PLI. Recent studies have drawn attention to the danger of metal pollution in lakes (Eid et al., 2012; Tao et al., 2012; Kükrer et al., 2015), dams (Loska and

☆ This study was extracted from part of Şakir Fural's PhD thesis entitled "Ecological Risk Analysis of İkizcetepeler Dam Lake Sediments (Balıkesir – Turkey)" completed at Department of Geography in Graduate School of Balıkesir University.

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https://doi.org/10.1016/j.ecolind.2020.106784
Received 8 May 2020; Received in revised form 24 July 2020; Accepted 29 July 2020
Available online 13 August 2020
1470-160X/

Wiechuła, 2003; Peraza et al., 2015; Kükrer and Mutlu, 2019), bays, lagoon and gulfs (Karakaya, 2011; Kükrer et al., 2020; Pehlivan, 2017; Cunningham, et al., 2019), streams (Brekhovskikh et al., 2002; Wang et al., 2018; Yao et al., 2019; Ustaoğlu and Tepe, 2019; Ustaoğlu et al., 2020; Ustaoğlu and Islam, 2020) river deltas (Engin, 2012; Zhang et al., 2016; Jorfi et al., 2017) and national parks (Sawicka and Rakowska, 1993; Yang et al., 2014). Since metals are not degraded by microbial and chemical processes, they cannot be purified in many treatment systems available with today's technology. This causes concern that anthropogenic metals may accumulate in the living cells of natural environments and pose a threat to the ecosystem health (Eid et al., 2012). Considering their severe toxic effects on the public and environmental health, the serious public scrutiny and concerns about ecological risks are justified (Tsakovski, et al., 2012).

According to the Ramsar report of Global Wetland Outlook 2018, 87% of wetlands in the world have disappeared in the last 300 years due to anthropogenic effects, while 35% disappeared between 1970 and 2018. As of 2007, while approximately one fifth of the world population (1.2 billion people) has no access to clean water, this ratio is expected to increase to 2/3 by 2025 (FAO, 2007). İkizcetepeler Dam Lake meets the drinking water, agricultural irrigation water and recreational fishing needs of the Balıkesir city centre, which had a population of 338.936 in 2018. Any ecological risk that may arise in the Dam Lake will directly affect people via the water network and in addition to causing health problems it will cause significant economic losses in agricultural irrigation and fishing (Ustaoğlu et al., 2020).

This study aimed to analyze the spatial distribution, potential ecological risks and possible sources of metals content in İkizcetepeler Dam Lake sediments using various ecological indices, multivariate statistical analyses, and geographic information systems software (GIS).

1.1. Materials and method

1.1.1. Study area

İkizcetepeler Dam Lake is located within the province borders of Balıkesir province in the south part of Marmara region (Fig. 1). Constructed in 1991 to meet the drinking and utility water needs of the city, the dam covers an area of 7.92 km^2 at normal water level. The 478.9 km^2 dam basin consists of four sub-basins: Kille stream, Koca stream, Çınarlı stream (Taşköy stream) and Bağırsak stream.

Table 1
Quality control results of ICP MS measurements using standard reference sample.

Element	Observed Value	Expected Value	Measurement Limits
As (ppm)	43.20	42.85	0.10
Al (%)	1.90	1.12	0.01
Cd (ppm)	2.48	2.37	0.01
Cr (ppm)	57.20	61.5	0.50
Cu (ppm)	141.66	149	0.01
Fe (%)	3.90	3.15	0.01
Hg (ppb)	266	260	5
Mn (ppm)	1.017	1.055	1
Ni (ppm)	80.60	77.78	0.10
Pb (ppm)	153.44	138	0.01
Zn (ppm)	345	345	0.10

1.1.2. Collection of sediment and rock samples

Sediment samples were taken from 32 locations whose coordinates were predetermined in a field study conducted at the Dam Lake in 2018 (Fig. 1). While determining the sampling points, the dam area was divided into 32 equal parcels, each covering an area of 0.25 km^2, so that each sampling point represented an area with the same measurement. The core sampling point was determined according to the sedimentary quality of the grab samples during the field study, while a core sample was taken from sampling point 18. Surface sediment samples were taken using a Van Veen Grab Sampler, and the core sample was taken with a Kajak Sediment Core Sampler. Rock samples were taken from seven points in the basin around the lake to determine lithologic background values. The two different background values from the rock and core samples were obtained (Table 2).

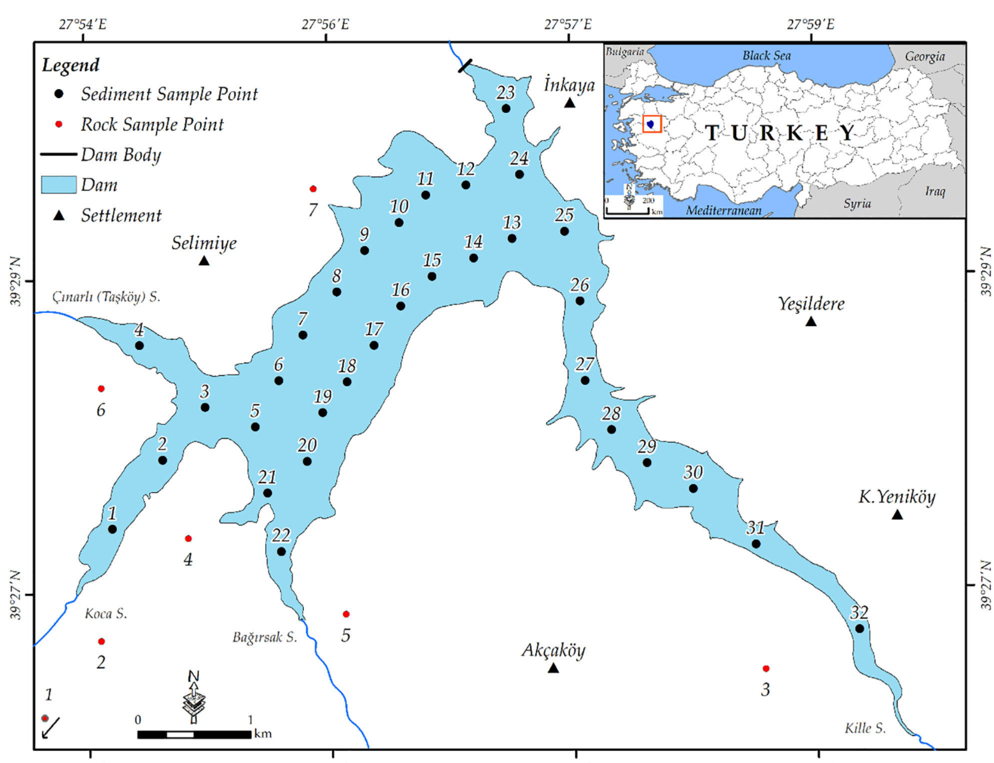

Fig. 1. Map of study area and sampling locations.

Table 2
Background (B.) values (ppm) of metals obtained from rocks and core sample slices.

Metal	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg
Lithologic B.	10.42	25.52	30.00	4.36	158.43	22.557	6.16	0.06	5.81	9.771	0.02
Core B.	17.77	27.87	52.80	36.70	587.00	27.400	27.40	0.17	26.00	22.700	0.06

1.1.3. Analytical procedures

Surface sediment and core samples, divided into 5 cm slices, were placed in petri dishes, dried at 60 °C for 24 h and crushed in a mortar as powder. OC analyses were performed using the Walkley Black Titration Method (Gaudette et al., 1974), and $CaCO_3$ analyses were performed using a Scheibler Calcimeter (Schlichting and Blume, 1966). Metal analyses were conducted using an ICP-MS device in Bureau Veritas Analytical Labs, Canada. Reference material, duplicate measurements and blind sample measurements were performed to test the validity and reliability of the metal analyses (Table 1). Analysis of CDP was carried out by applying the acetone extraction method to wet sediment samples, followed by the spectrophotometric method (Lorenzen, 1971). EF, CF and I_{geo} were used to detect metal deposits of anthropogenic origin. The EF was calculated this formula:

$$EF = \left[\frac{Cn\ sample}{CAl\ sample}\right] / \left[\frac{Bn\ Background}{B\ Al\ Backgrond}\right]$$

where C_n is as before; C_{Al} is the aluminum concentration, B_n background metal, B_{Al} is background Al. The obtained results were evaluated as follows: EF < 2 deficiency to minimal enrichment, EF = 2–5 moderate enrichment, EF = 5–20 significant enrichment, EF = 20–40 very high enrichment and EF > 40 extremely high enrichment (Sutherland, 2000).

CF was calculated this formula:

$$CF = \frac{Metal\ concentration}{Metal\ background\ value}$$

The obtained results were evaluated as follows: CF < 1 low contamination, 1 ≤ CF < 3 moderate contamination, 3 ≤ CF < 6 high contamination, and CF > 6 very high contamination (Hakanson, 1980).

I_{geo} is an ecological risk index that evaluates the level of pollution caused by metals and whether the source is based on natural or anthropogenic effects. I_{geo} calculations were performed according to the Müller Method (Müller, 1969). Thus:

$$Igeo = \log_2 \frac{Cm}{(Bm * 1.5)}$$

where *Cm* is corresponds to the amount of metal measured; and *Bm* is corresponds to the continental crust value of the metal. The data obtained were evaluated as follows: I_{geo} ≤ 0 uncontaminated, 0 < I_{geo} < 1 uncontaminated to moderately contaminated, 1 < I_{geo} < 2 moderately contaminated, 2 < Igeo < 3 moderately contaminated to strongly contaminated, 3 < I_{geo} < 4 strongly contaminated, 4 < I_{geo} < 5 strongly contaminated to extremely contaminated, I_{geo} ≥ 5 extremely contaminated (Müller, 1969).

PLI was used to calculate the quality of the sediments based on their metal values (Tomlinson et al., 1980) as follows:

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

CF represents the contamination factor and n represents the number of elements used. The normal PLI value in the sediment was determined to be 0, and this value indicates that there is no pollution, but the risk of pollution will rise if the value of 1 is exceeded (Suresh et al., 2011).

TRI was used to determine the toxic effects of metals. In the formula, TRI is the toxic risk index of a single metal, C_i shows the metal concentration in the sediment sample, and n is the number of metals (Zhang et al., 2016). TEL is the threshold effect level, and PEL is the probable effect level (Macdonald et al., 1997).

$$TRI_i = \sqrt{\frac{(C_i/TEL)^2 + (C_i/PEL)^2)}{2}}$$

The sum of the individual TRI_i values for the metals yields the integrated TRI thus:

$$TRI = \sum_{i=1}^{n} = TRI_i$$

TRI data were evaluated as follows: TRI ≤ 5 no toxic risk, 5 < TRI ≤ 10 low toxic risk, 10 < TRI ≤ 15 moderate toxic risk, 15 < TRI ≤ 20 considerable toxic risk, and TRI > 20 very high toxic risk.

The mPER index was used to determine the ecological risk level of the metals. In this context, individual mER and integrated modified ecological risk analysis (mPER) were performed for each metal. CF is generally used in ecological risk and potential ecological risk calculations (Hakanson, 1980). However, since there is no geochemical normalization with Al or Fe in CF calculations, errors from grain size are not minimized. Therefore, mER using EF in ecological risk calculations was developed (Brady et al., 2015).

mER was calculated thus:

$$mER = EF \times Tr^i$$

In this formula, EF is the enrichment factor and Tr^i is the toxic risk coefficient of the metal. The results were evaluated as follows: mEr < 40 low potential ecological risk, 40 ≤ mEr < 80 moderate potential ecological risk, 80 ≤ mEr < 160 significant potential ecological risk, 160 ≤ mEr < 320 high potential ecological risk, and mEr ≥ 320 very high potential ecological risk (Hakanson, 1980).

In the study, mPER was calculated using the following formula:

$$mPER = \Sigma\ mER$$

mPER is the sum of the mER values of metals. The results were evaluated as follows: mPER < 150 low ecological risk, 150 ≤ mPER < 300 moderate ecological risk, 300 ≤ mPER < 600 significant ecological risk, mPER ≥ 600 very high ecological risk (Hakanson, 1980).

2. Results and discussion

2.1. Spatial distribution of metals in Dam Lake base

Metal concentration in the İkizcetepeler Dam Lake base changes under the influence of streams. Depending on natural and anthropogenic effects in their basins, streams discharge different types and concentrations of metals into the dam (Fig. 2). Aluminum was detected in maximum concentration (30.000 ppm) at the sampling points in the Kille stream estuary and the middle part of the dam and in minimum concentration (11.000 ppm) in the estuaries of other streams. Arsenic was detected at maximum level (37 ppm) at the sampling points in the middle part of the dam, and at minimum level (15 ppm) in the estuaries of Kille stream and Bağırsak stream. Copper was found to peak at (22 ppm) in the inner parts and estuaries of Kille stream and Bağırsak stream and to plunge to 10 ppm level in the estuaries of Koca stream and Çınarlı stream (Taşköy stream). Mercury reached its maximum of

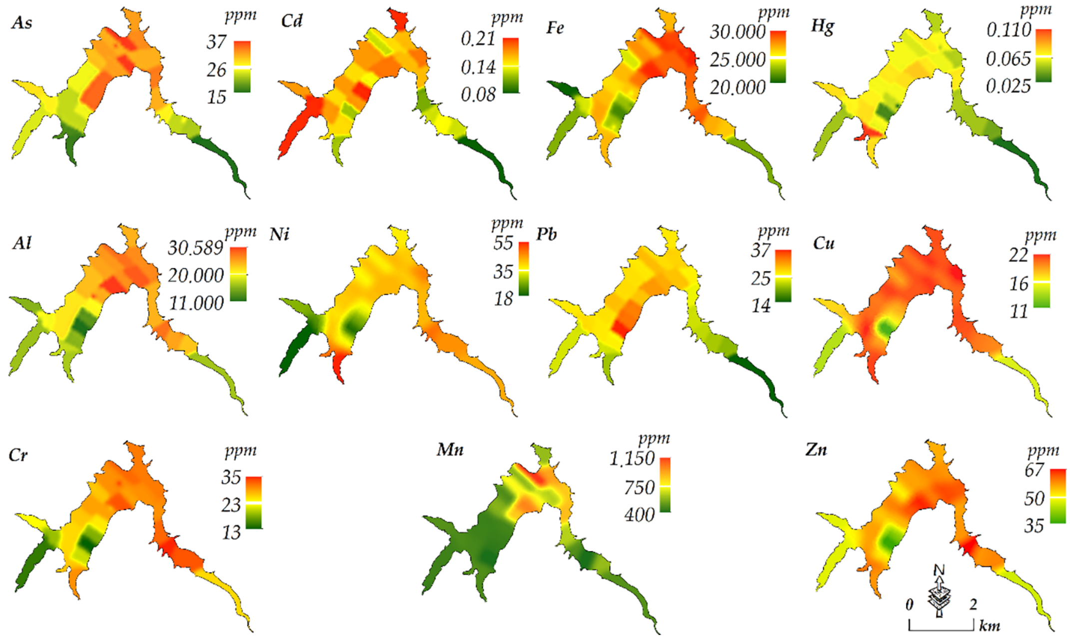

Fig. 2. Spatial distribution of metals in the dam base based on kriging interpolation.

0.110 ppm in the estuary of Bağırsak stream and its minimum of 0.025 ppm in the estuaries of Kille stream and Koca stream and also in the estuary of Çınarlı stream (0.055 ppm). Zinc was found to peak at 67 ppm in the estuaries of Kille stream and Bağırsak stream. It was in the range of 48–63 ppm in the estuaries of Koca stream and Çınarlı stream and also in inner areas. Iron was found to vary between 26.000 and 30.000 ppm in the estuaries of Kille stream and Bağırsak between 20.000 and 22.000 ppm in the estuaries of Kille stream and Bağırsak stream, and between 24.000 and 30.000 ppm in the inner areas (Fig. 2). Cadmium peaked at 0.21 ppm in the estuaries of Koca stream and Çınarlı stream while it was at minimum level (0.008 ppm) in the estuaries of Kille stream and Bağırsak stream. Maximum and minimum Cr was 35 ppm in the estuaries of Kille stream and Bağırsak stream and 12 ppm in the estuary of Koca stream respectively.

Around the sampling point 19, with a water resource, Pb reached its maximum of 37 ppm and its minimum of 14 ppm in the estuaries of Koca stream, Kille stream and Bağırsak stream. Manganese plummeted to 400 ppm in the estuaries of all streams and throughout the inner parts of picked at 1.140 ppm in the estuary of Kireçli stream. The minimum and maximum Ni was estimated at 17 ppm in the estuaries of Koca stream and Çınarlı stream and at 55 ppm in the estuary of Bağırsak stream respectively. Metal concentrations of some wetlands including this study are compared in Table 3.

2.2. Spatial distribution of organic carbon (OC), chlorophyll degradation products (CDP) and calcium carbonate ($CaCO_3$) in the Dam Lake base

Marine and freshwater ecosystems accommodate 20% of the global TOC pool (Siegenthaler and Sarmiento, 1993). While OC concentration at natural levels is not harmful to the ecosystem, anthropogenic inputs from domestic and industrial usage causes organic matter pollution (Xu, et al., 2019). Organic materials play an important role in the transportation of metals (Tomlinson et al., 1980; Yang et al., 2014). Therefore, it is important to determine the spatial distribution of OC in order to understand the metal transport processes. OC concentration in İkizcetepeler Dam Lake generally increases in the estuaries of streams. OC was detected at a maximum level (3%) at the sampling points in the estuaries of Koca stream, Kille stream and Çınarlı stream and at a minimum level (0.5%) in the estuary of Bağırsak stream and throughout its inner parts (Fig. 3a). According to various other lakes in the current literature, the OC concentration in the İkizcetepeler Dam Lake is at normal levels (Table 4). CDP provides information about the vegetal production processes in the Dam Lake (Cabrita et al., 2018). CDP ranged from 150 µg/g in the estuary of Kille stream 50–75 µg/g in the estuary of Çınarlı stream and Koca stream and to 0.25 µg/g in the estuary of Bağırsak stream (Fig. 3b). These values demonstrate that the CDP was discharged into the dam by streams other than Bağırsak stream and disperse to the inner parts (Fig. 3b). $CaCO_3$ is an important indicator in determining the transportation processes of metals (Shetye et al., 2009). $CaCO_3$ concentration was around 12% in the estuary of Çınarlı stream, in the range of 6–8% in the estuaries of Kille stream and Koca stream, and at its minimum 2% in the estuary of Bağırsak stream. According to spatial analysis, $CaCO_3$ was discharged by Çınarlı stream, Koca stream, and Kille stream (Fig. 3c).

2.3. Spatial distribution of enrichment factor (EF) in Dam Lake base

Based on the lithologic background values, EF was of the following order: Ni > As > Cr > Mn > Hg > Cd > Pb > Cu > Zn > Fe. In the İkizcetepeler Dam Lake, enrichment was detected as significant for Ni, as moderate for As, Cr, Mn, Hg and Cd and as low for Pb, Cu, Zn and Fe. According to field studies and spatial analysis of the lake basin, the likely source of Ni enrichment is a mining quarry located on the border between Koca stream and Bağırsak stream. The main anthropogenic sources of moderately enriched As around the sampling point 19 were chemical fertilizers, geothermal sources and fossil fuel use (Atabey, 2009). There are large agricultural areas near the sampling point 19 and a water source exists at the dam base. In this case, the probable source of As is agricultural activity and lithologic formations through which the water source passes. Chromium is moderately enriched in all estuaries except Koca stream. Chromium is thought to be generated from agriculture in the basin, domestic wastes and factories working with metallic raw materials in Çınarlı stream basin. Vehicle fuels, accumulators, batteries and paint are the most important Pb sources. Bullet is carried into water ecosystems by atmospheric events and streams (Dündar and Arslan, 2005). However, Pb enrichment at the bottom of the dam reached its highest value at the sampling point 19, which enables discharge into the water source according to the 1:25.000 scale J19b2 topography map prepared in 1980. Mercury is moderately enriched in the estuary of Bağırsak stream. The main

Table 3
Minimum and maximum metal concentrations of some Dam Lake in the literature (ppm).

LKS	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
İkizcetepeler Dam Lake (This study)	10.170	16.6	0.09	12.80	10.60	20.000	25.00	402	16.50	14.68	33.45
	20.520	32.9	0.19	30.00	22.20	30.020	108.00	1.159	54.70	36.56	65.65
Avşar Dam Lake[1] (Turkey)			0.34	9.40	18.20	19.680			19.80	0.64	
			1.23	19.90	38.40	28.500			39.40	6.35	
Seyhan Dam Lake[2] (Turkey)			1.55	84.90	12.40	30.640		595			32.80
			2.44	135.50	23.80	43.204		904			43.30
Kapulukaya Dam Lake[3] (Turkey)		9.10	0.50	98.10	9.80		1.01	326.6	24.70	8.60	14.80
		69.70	1.80	1.116	29.30		1.60	1.053	127.15	34.14	124.24
Karacaören I Dam Lake[4] (Turkey)	1.949			13.50	7.80	7.217		308.20	97.55	1.69	13.95
	5.847		0.93	64.50	81.55	15.584		634.90	187.20	301.14	59.11
Yamula Dam Lake[5] (Turkey)			3.70	2.60	4.75			45.80	3.77	4.73	6.73
			4.80	19.80	12.50			341.30	42.67	12.15	33.97
Umurbey Dam Lake[6](Turkey)			0.001		0.023	2.060		0.331		0.006	0.162
			0.006		0.095	9.404		0.953		0.052	2.778
Çatören Dam Lake[7]	3.500	0.001		30.10	18.50	1.950		112	7.50	12.50	19.23
	13.000	0.01	0.70	140.7	42.20	12.500		425	38.25	26.83	42.41
(Turkey) Asartepe Dam Lake[8] (Turkey)			0.76	0.58	10.63	269.90		3.34		17.73	44.25
			1.33	1.63	18.70	708.80		5.96		21.90	60.37
Rybnick Dam Lake[9] (Poland)			20.48		122.37				51.87		
			51.07		671.7				117.80		
Klingenberg Dam Lake[10]		10.6	2.48	1.73	5.62	1.71		3.54	6.32	2.63	88.6
		13.6	167	3.07	15.10	23.02		5.09	112.20	22.60	3.281
(Germany) Aguamilpa Dam Lake[11] (Mexican)	7.760			0.22	0.79	4.740			0.24		14.8
	27.600		0.27	18.3	60.8	15.900	0.04		189	13.6	51.8

[1] Özözen (2005),
[2] Çevik et al. (2009),
[3] Başaran (2010),
[4] Erdoğan (2014),
[5] Kar (2011),
[6] Selvi (2012),
[7] Çiftçi (2015),
[8] Tunç (2015),
[9] Loska et al. (1997),
[10] Hahn et al. (2018),
[11] Peraza et al. (2015).

anthropogenic sources of Hg are fossil fuels, industrial wastes, cement and metal factories. Mercury enters aquatic ecosystems from atmospheric events and streams. The moderate level of Hg enrichment in the dam occurs in a rather local area. During field trips to identify the Hg source, rock samples were taken from the area and the source was determined to be of lithologic origin. Cadmium was moderately enriched in the estuaries of Koca stream and Çınarlı stream and at the sampling points 17, 18, 19 and 20. The main reason for this is intensive agricultural activity at the mentioned points because Cd is the raw material of phosphate fertilizers (Bolat and Kara, 2017). Table 5 shows the enrichment factors of some wetlands in the current literature. The spatial distribution of the enrichment factor at the base of the dam is given in Fig. 4.

Table 4
Organic carbon concentrations identified in some studies in the literature.

Lake	OC (%)	References
İkizcetepeler Dam	0.11–3.03	Fural et al. (2019)
Çıldır Lake (Turkey)	0.15–2.50	Kükrer et al. (2015)
Aygır Lake (Turkey)	0.34–13.90	Kükrer (2018)
Aktaş Lake (Turkey)	0.13–9.80	Kükrer (2017)
Tortum Lake (Turkey)	0.0–0.50	Kükrer (2016)
Uzunçayır Dam (Turkey)	4.20–8.30	Kutlu (2018)
Sarbsko Dam (Poland)	0.30–18.50	Woszczyk et al. (2011)
Caohai Lake (China)	8–25	Jiang et al. (2018)
Wujiangdu Lake (China)	20–42	Jiang et al. (2018)
Honfong Lake (China)	15–24	Jiang et al. (2018)
Biwa Lake (Japan)	10–20	Ishiwatari et al. (2009)

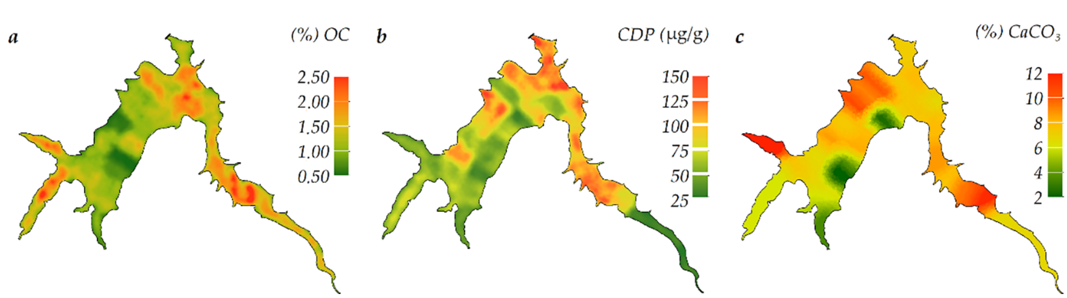

Fig. 3. a: Spatial distribution of organic carbon amount on the dam base, 3b: Spatial distribution of chlorophyll decomposition products, 3c: Spatial distribution of $CaCO_3$ based on kriging interpolation (without scale).

Table 5
Comparison of enrichment factor (EF) of some dams (D) and lakes (L) in the current literature.

Location		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
İkizcetepeler D.	(This Study)	3.88	2.04	2.86	1.15	2.34	6.93	0.48	1.08
Gökçekaya D.[1]	(Turkey)	46.13	0.25	7.58	6.54		5.77	23.59	13.09
Uzunçayır D.[2]	(Turkey)		1.61	1.61	0.97	0.07	5.27	0.83	0.97
Seyhan D.[3]	(Turkey)		8.55	1.91	0.41				0.55
Kapulukaya D.[4]	(Turkey)	47.35	1.89	3.42	18.51	0.64	24.44	1.13	7.03
Aguamilpa D.[5]	(Mexican)		4.04	0.31	0.61	0.46	1.55	1.22	1.11
Rybnick D.[6]	(Poland)		28.32	15.94	39.58		37.65	35.38	64.11
Aygır L.[7]	(Turkey)	0.80	0.90	1.50	0.60	0.55	0.70	1.30	2.70
Tortum L.[8]	(Turkey)	1.35	1.79	1.01	1.06	1.19	1.07	1.34	1.04
Çıldır L.[9]	(Turkey)	1.10	1.25	0.85	0.75	1.80	0.60	0.80	0.75

[1] Kırmızıgül (2013),
[2] Kutlu (2018),
[3] Çevik (2009),
[4] Başaran (2010),
[5] Peraza et al. (2015),
[6] Loska and Wiechuła (2003),
[7] Kükrer (2018),
[8] Kükrer (2016),
[9] Kükrer et al. (2015).

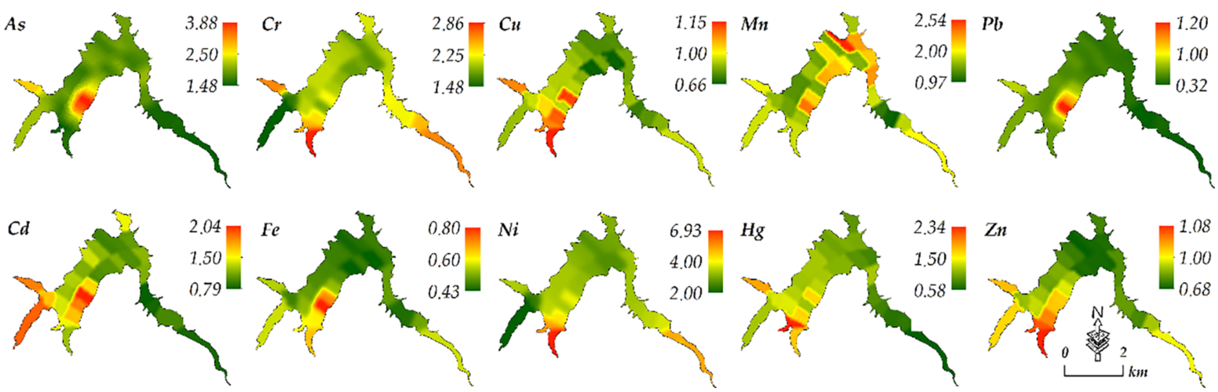

Fig. 4. Spatial distribution of enrichment factor in dam base according to lithologic background values and kriging interpolation.

Table 6
Comparison of contamination factor (CF) and PLI in dams and lakes worldwide and in Turkey in the current literature.

Location	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	PLI
İkizcetepeler D. (This study)	2.32	4.65	2.77	4.73	1.92	1.18	2.61	3.85	8.83	1.04	1.85	1.44
Uzun Çayır D.[1] (Turkey)		5.04	1.09	1.08	0.65	0.67	0.04	0.74	3.49	0.56	0.66	0.62
Aguamilpa D.[2] (Mexican)	0.41		1.61	0.14	0.29	0.44	0.15	1.11	0.78	0.45	0.41	0.41
Tailing D.[3] (Ghana)		0.90	23.70	0.04	0.20					0.10	0.04	0.11
Weija D.[4] (Ghana)			0.22			6.55		0.02		0.09		6.18
Asartepe D.[5] (Turkey)				4.37		2.14		2.92	3.99		2.96	3.32
Nasser Lake[6] (Egypt)			0.58	0.32	0.54	0.26		0.29	0.41	0.54	0.37	
Tortum Lake[7] (Turkey)	0.81	1.03	1.22	0.82	0.77	0.84	0.89	0.86	0.82	0.99	0.82	0.15
Çıldır Lake[8] (Turkey)	1.60	1.50	1.60	1.10	1.00	1.00	2.90	1.10	0.90	1.20	1.10	1.90
Beyşehir Lake[9] (Turkey)	1.28	3.66		2.28	2.15	1.94		2.27	5.25		2.11	

[1] Kutlu (2018),
[2] Peraza et al. (2015),
[3] Sey and Belford (2019),
[4] Raphael et al. (2016),
[5] Tunç (2015),
[6] Goher et al. (2014),,
[7] Kükrer (2016),
[8] Kükrer et al. (2015),
[9] Tunca (2016).

2.4. Spatial distribution of contamination factor (CF) in Dam Lake base

The CF may be sequenced thus: Ni > Cr > As > Mn > Cd > Hg > Al > Cu > Zn > Fe > Pb according to the lithologic background values. Contamination was detected at a moderate level for Cu, Fe, Pb and Zn, at a high level for Cr, As, Hg, Cd and Al and at a very high level Mn and Ni. Possible sources of Ni, As, Cr, Mn, Hg, Cd and Pb were accounted for by EF. The CF determined that Cu, Fe, Zn and Al were also affected by anthropogenic activities. Al, Cu, Fe and Zn constitute the raw materials of fertilizers used in plant nutrition (Bolat and

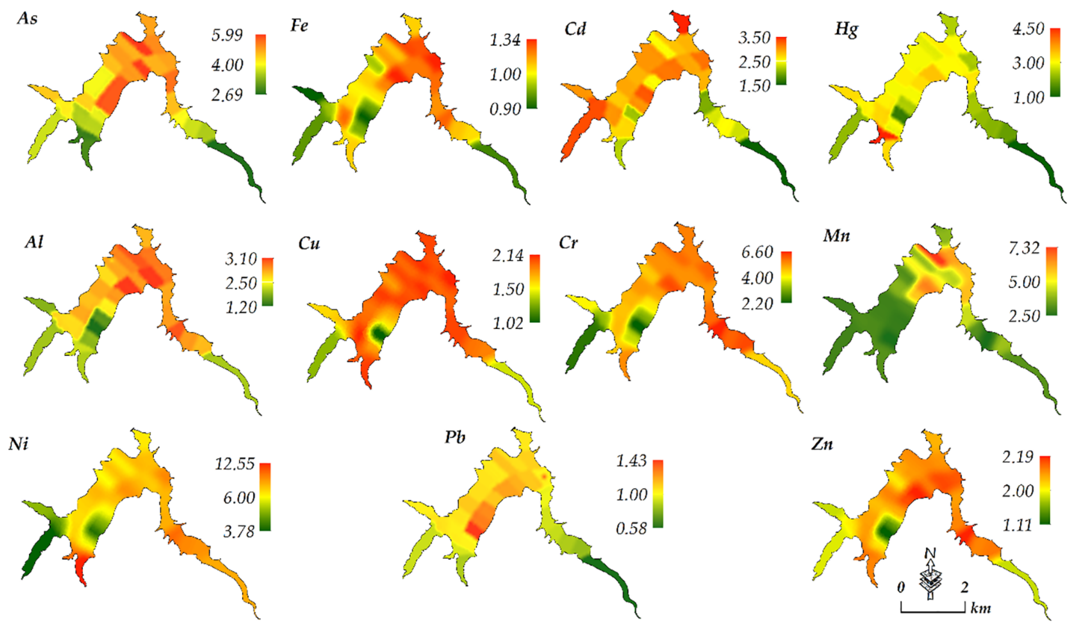

Fig. 5. Spatial distribution of contamination factor in dam base according to lithologic background values and kriging interpolation.

Kara, 2017). Agricultural activities carried out in the Dam Lake basin are considered as an anthropogenic activity that increases the contamination factor of the mentioned metals. The contamination factor of some wetlands is shown in Table 6. The spatial distribution of the contamination factor on the Dam Lake floor is shown in Fig. 5.

2.5. Geoaccumulation index (I_{geo})

According to lithologic background values, I_{geo} showed the descending level of pollution thus: Ni > Cr > As > Mn > Cd > Hg > Cu > Zn > Fe > Pb. The Dam Lake; was not contaminated with Fe and Pb, contaminated with Al, Cd, Cu, Hg and Zn, at low levels contaminated with As and Cr and moderately at the lower limits and contaminated with Ni moderately (see Fig. 6).

2.6. Spatial distribution of pollution load index (PLI) and toxic risk index (TRI) in the Dam Lake base

PLI ranged from 0 to 13. The estuaries of Bağırsak stream and Çınarlı stream (Taşköy stream) and sampling points 18, 19 and 20 were

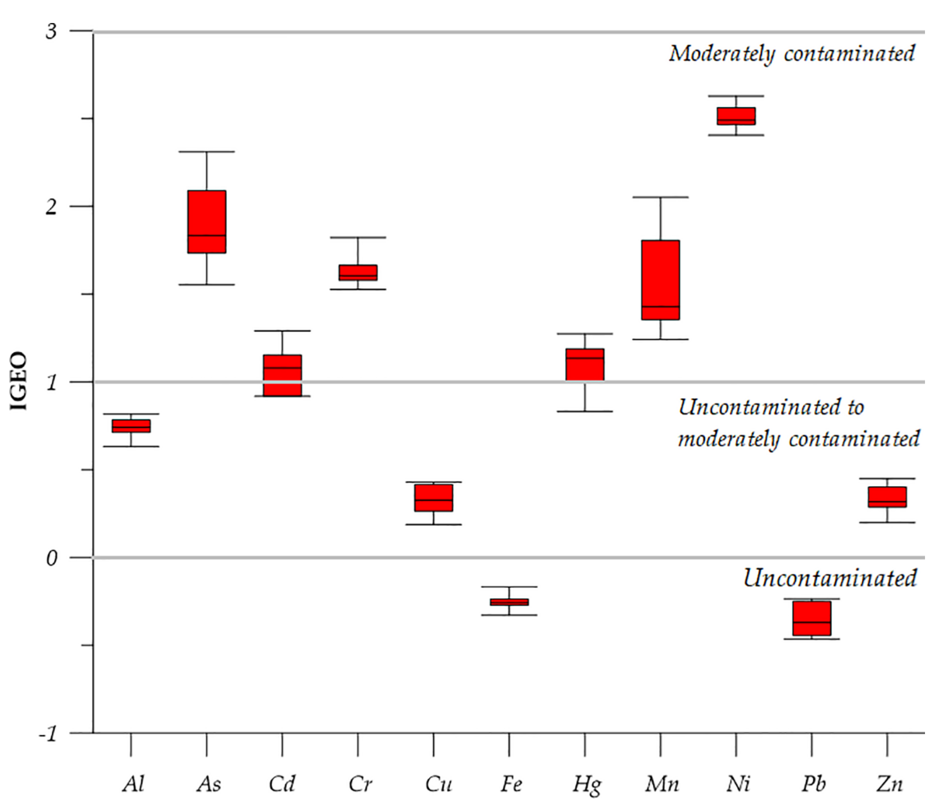

Fig. 6. Box Whisker plot of geoaccumulation index according to lithologic background values.

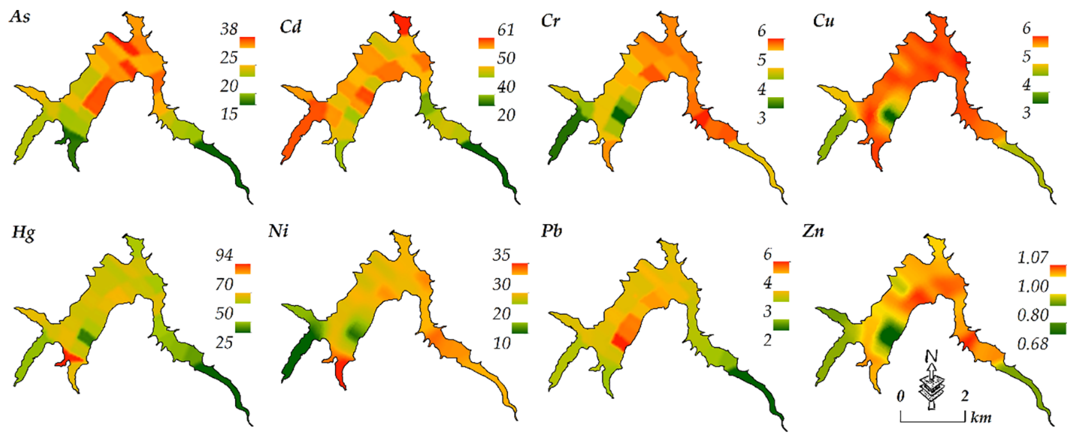

Fig. 7. Spatial distribution of ecological risk (mER) in the dam base according to lithologic background values.

identified as areas at a risk of pollution (Fig. 8a). Their common feature of these is the existence of large agricultural areas near the sampling points. Table 6 presents the PLI values of the study area and related literature. TRI varies between 4.00 and 6.60. No toxic risk was detected at sampling points 1 and 2 in the estuary of Koca stream, at the sampling points 19 and 20 near the water source, and sampling points 31 and 32 in the estuary of Kille stream. A low toxic risk was detected at the other points (Fig. 8c).

2.7. Spatial and vertical distribution of ecological risk index (mER) and potential ecological risk index (mPER) in the Dam Lake base

mER and mPER were calculated separately based on the lithologic background values obtained from rock samples and background values obtained from core sample data. In addition, the vertical distribution of mPER in the core sample was calculated according to the core sample and lithologic background data; by which means the temporal change was examined. The ecological risk at İkizcetepeler Dam was of the descending order: Hg > Cd > As > Ni > Cu > Cr > Pb > Zn according to lithologic background values and Hg > Cd > As > Ni > Cu > Pb > Cr > Zn in accordance with core sample background values. As shown by lithologic background values, the ecological risk level was identified as significant for Hg, as moderate level for Cd, as very close to moderate for As and Ni, and as low for the other metals (Fig. 7). From the obtained core sample background values, the ecological risk level was identified for Hg at the lowest segment of significant level, as moderate Cd, and as low for other metals.

mPER varies between 50 and 123 according to the core sample background values and between 98 and 201 according to the lithologic background values. The core sample background values indicate that a low ecological risk was detected in the Dam Lake. According to the lithologic background values, a low level ecological risk was found in the estuaries of Kille stream and Çınarlı stream and around sampling point 19; potential ecological risk was identified at other points.

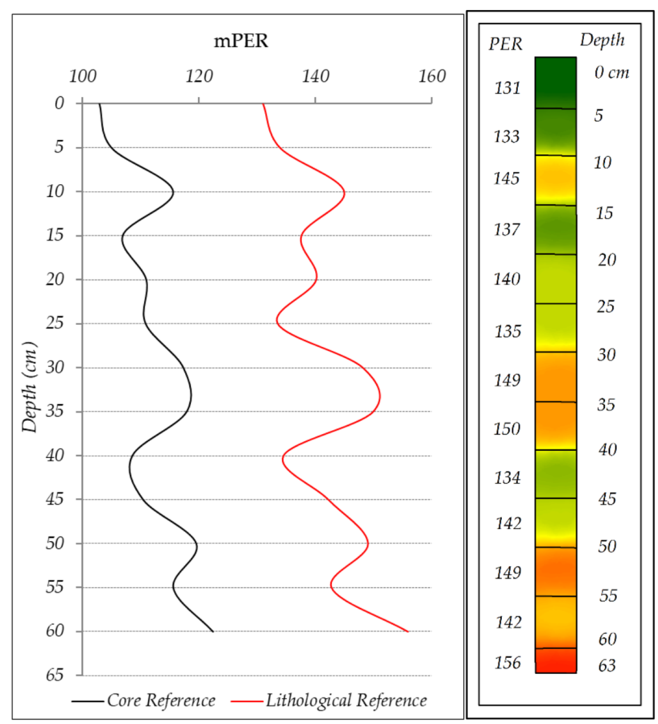

Fig. 9. Vertical distribution of potential ecological risk (mPER) according to core sample and lithologic background values.

Temporal change of mPER varied between 102 and 123 as per the core sample background values and between 131 and 156 according to lithologic background values. When the temporal change of potential ecological risk was analyzed, a downward trend was observed (Fig. 9). The mER of some wetlands is shown in Table 7.

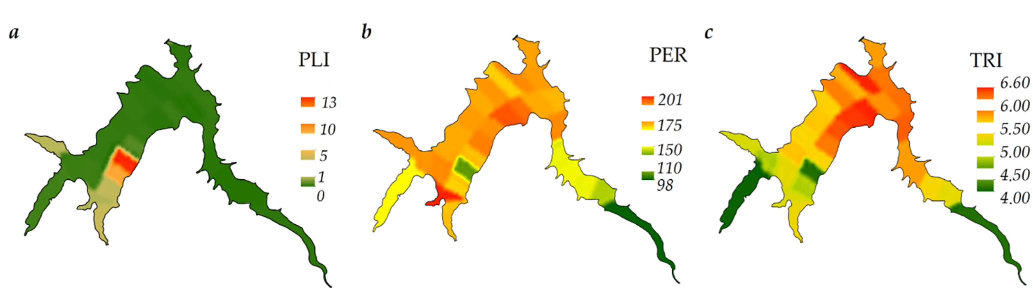

Fig. 8. a: Distribution of pollution load index (PLI) in dam base, 8b: Distribution of potential ecological risk (mPER), 8c: Distribution of toxic ecological risk (TRI) (According to lithologic background values) (without scale).

Table 7
Comparison of ecological risk index (mER) and potential ecological risk index (mPER) of some dams (D) and lakes (L).

Location		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	PER
İkizcetepeler D.	(This study)	38	61	5.72	5.98	94	35	5.68	1.07	201
Uzun Çayır D.[1]	(Turkey)	50.44	32.85	2.15	3.26	1.92	17.77	2.82	0.65	111
D. Duze D.[2]	(Poland)	96.14	2532	2.55	13.01		12.46	45.65	25.55	2727
Tailings D.[3]	(Ghana)	9.65	711	0.10	1.20			0.50	0.04	722
T. Georges D.[4]	(China)		64	1.69	10.45	64	2.41	2.72	2.15	147
Hubei L.[5]	(China)	16.90	97.11	2.50	8.60	78	2.67	7.15	1.95	215
Dali L.[5]	(China)	35	96	30	30			35	10	236
Aygır L.[6]	(Turkey)	12	40	5	5	26	6	8	5	107
Tortum L.[7]	(Turkey)	14	40	2	6	50	5	6	2	125
Çıldır L.[8]	(Turkey)	15	50	6	7	110	10	9	6	213

[1] Kutlu (2018),
[2] Tytła and Kostecki (2019),
[3] Sey and Belford (2019),
[4] Liu et al. (2015),
[5] Xu, et al. (2019),
[6] Kükrer (2018),
[7] Kükrer (2016),
[8] Kükrer et al. (2015).

2.8. Multivariate statistical analysis

Pearson's correlation matrix analysis was carried out to identify possible sources of metals and their transport processes as strong positive correlations were detected between some metals. This shows that the sources and transportation processes of these metals are similar (Wang et al., 2018). Organic materials play an active role in the transportation of metals, so correlations between organic materials and metals should be examined (Zhang et al., 2016). A positive correlation was found between OC and Zn and Al and $CaCO_3$. Spatial distribution maps show that the areas where these metals and the OC input are found at their highest amounts are the sampling points corresponding to the estuary of Kille stream (Fig. 2). CDP exhibited a positive correlation with Cu, Zn, Fe, Cr, Al, and $CaCO_3$. This indicates that CDP and the metals mentioned are carried from terrestrial sources by the Bağırsak stream (Fig. 2).

Another important indicator in determining the transportation processes of metals is the amount of $CaCO_3$ (Shetye et al., 2009). $CaCO_3$ showed a positive correlation with Cu, Zn, Cr, Al, OC and CDP. These metals were discharged together with $CaCO_3$ from terrestrial sources by Çınarlı stream and Bağırsak stream (Fig. 2). According to the correlation analysis data of the metals, it was determined that *Cu* showed positive correlations with Zn, Ni, Mn, Fe, Cr, Al, Hg, CDP and $CaCO_3$. Positive correlations were found between Pb and Ni, As, Cd, Hg; between Zn and Ni, Mn, Fe, Cr, Al, Hg, OC, CDP and $CaCO_3$; between Ni and Mn, Fe, Cr, Al; between Mn and Fe, As, Cr, Al; between Fe and As, Cr, Al, Hg, CDP; between As and Cd, Al; between Cd and Hg; between Cr and Al, CDP, $CaCO_3$ and between Al and OC, CDP, $CaCO_3$ (Table 8). According to the analysis, most of the metals show positive correlation with each other. However, Pb, As and Cd had very little association with other metals. This shows that the source and transportation processes of these metals are different (see Table 9).

Table 9
Factor analysis. (Bold values indicate a high relationship between variables).

	Factor 1	*Factor 2*	*Factor 3*	*Factor 4*
Cu	**0.853928**	−0.0303204	0.194867	0.397755
Pb	−0.224637	**0.80313**	−0.274914	0.195405
Zn	**0.896884**	−0.0805418	0.190827	0.261009
Ni	**0.857477**	−0.428104	−0.0647929	0.0372676
Mn	**0.688694**	0.505175	−0.058413	−0.141827
Fe	**0.936917**	0.241223	0.0116765	0.0487253
As	0.242775	**0.893156**	0.171107	0.00462371
Cd	−0.0968883	0.603125	0.171858	**0.622958**
Cr	**0.912819**	−0.151059	0.285135	−0.0326642
Al	**0.853956**	0.276288	0.333895	0.00313544
Hg	0.2859	0.0675688	−0.137454	**0.87211**
OC	0.0568623	0.0303492	**0.764316**	−0.00113031
CDP	0.361289	0.110749	**0.658135**	−0.163667
CaCO3	0.0639325	−0.111539	**0.894221**	0.0746469

Bullet and As reached their highest enrichment around the sampling point 19. The 1/25.000 scale topography map of the area, prepared before the dam was built, points to a water source at the specified location. According to correlation analysis and spatial distribution maps, Pb and As discharges arise from the mentioned source. One of the most

Table 8
Pearson correlation coefficients between variables. (Bold values indicate high correlations).

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg	OC	CDP	CaCO3
Cu														
Pb	−0.1297													
Zn	**0.8973**	−0.2026												
Ni	**0.7720**	**−0.3659**	**0.7596**											
Mn	**0.4545**	0.1254	**0.4950**	**0.3725**										
Fe	**0.7695**	0.0533	**0.8432**	**0.6942**	**0.7190**									
As	0.2272	**0.6680**	0.1357	−0.1103	**0.5521**	**0.3737**								
Cd	0.2402	**0.6021**	0.1360	−0.2758	0.1277	0.1426	**0.5394**							
Cr	**0.8663**	−0.3242	**0.8666**	**0.8991**	**0.5148**	**0.7569**	0.1367	−0.0867						
Al	**0.7930**	−0.0367	**0.8771**	**0.6180**	**0.6604**	**0.8722**	**0.4310**	0.2124	**0.8361**					
Hg	**0.6002**	**0.3906**	**0.4742**	0.2443	0.2302	**0.3681**	0.2628	**0.5731**	0.2638	0.2959				
OC	0.1889	−0.2541	**0.3773**	0.1164	0.1776	0.1930	0.0449	0.0341	0.3277	**0.4361**	0.0113			
CDP	**0.4915**	−0.0297	**0.4342**	0.2155	0.2080	**0.4303**	0.3577	0.2265	**0.4466**	**0.5655**	0.1301	0.2814		
$CaCO_3$	**0.4491**	−0.3010	**0.3651**	0.2017	0.0024	0.0939	0.1622	0.0970	**0.4384**	**0.4109**	0.0884	**0.5078**	**0.6149**	

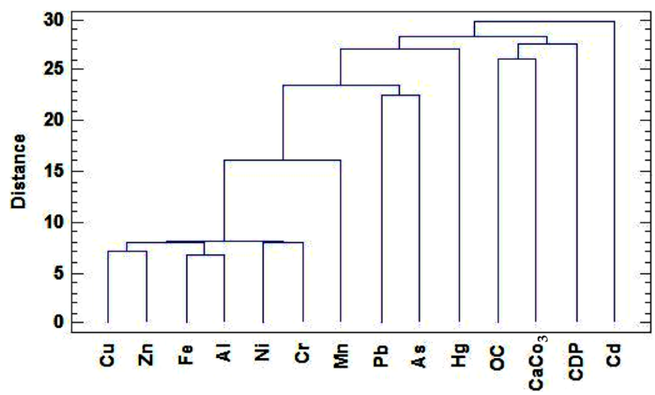

Fig. 10. Cluster analysis.

important sources of As and Pb is other volcanic rocks and carbonated rocks, especially pyrite (Atabey, 2009). Limestone and andesite formations are located near the sampling point 19. In this case, the possible source of Pb and As discharge to the dam related to the lithogenic factors. Cd was discharged by streams from Koca stream and Çınarlı stream basin.

Four components were calculated for PCA analysis. These components explained 83.41% of the total change. The first factor is responsible for 42.92% of the change and consisted of Cu, Zn, Ni, Mn, Fe, Cr, and Al. These metals, which were found to act together in the correlation analysis and spatial distribution maps (Fig. 2), are of terrestrial origin. The second factor elucidated 18.43% of the changes and consisted of Pb and As. These are also determined to have similar sources in the correlation analysis and spatial distribution maps and are discharged by the water source at the bottom of the dam, possibly of lithogenic origin. Component 3, which included OC, CDP, and $CaCO_3$, accounted for 13.49% of the total change. Cadmium and Hg in factor 4 were discharged from a different source than the other inputs. When the spatial distribution maps were examined, Cd was found to be discharged from Koca stream and Çınarlı stream basins, where intensive agriculture is carried out. Hg discharge is of lithologic origin, which is evidenced by rock samples taken from the region. The average Hg concentration was 0.024 ppm in the rock samples taken from seven different points in the basin. However, Hg concentration was determined as 0.101 ppm in the 4th lithologic sample taken from sampling point 21 where Hg creates a significant ecological risk. This value indicates that the lithologic-origin Hg concentration in the area was 4 times the average. Hg concentration was 0.011 ppm on average in the 6 samples outside the 4th lithologic sampling point. In this case, the Hg concentration detected at the 4th lithologic sampling point was 10 times the other points.

According to the cluster analysis data, Cu, Fe, Zn, Al, Ni, Cr, and Mn were transferred from a common source. As shown on the spatial distribution maps, these metals were transported from the land by streams (Fig. 2). OC, CDP, and $CaCO_3$ were also transported from terrestrial sources by different streams. Pb and As were discharged from a water source, Hg was discharged due to its lithologic features, and Cd was discharged into the dam from Koca stream and Çınarlı stream basin (Fig. 10). Cluster analysis data were consistent with the spatial distribution maps, the correlation analysis, and the factor analysis.

3. Conclusion

Our findings show that Hg posed a significant ecological risk, Cd a moderate ecological risk, As and Ni a close-to-moderate ecological risk, and the other metals exhibited a low ecological risk based on the lithologic background values. In relation to the core sample background values, Hg was at the lower limits of the significant ecological risk level, Cd was at moderate ecological risk level and no ecological risk was identified for the other metals. TRI analysis showed a low toxic risk in the Dam Lake. Metals that may create an ecological risk for the Dam Lake were identified as Hg, Cd, As and Ni. While multivariate statistical analyses and spatial distribution maps indicated Hg and As of lithologic origin and Cd and Ni as of anthropogenic origin. The probable source was fertilizers used on agricultural land for Cd and mining quarry located at the intersection of Bağırsak stream basin and Koca stream basin for Ni. The risk decreased in the present day according to the vertical distribution of the potential ecological risk. However, it is necessary to keep other anthropogenic activities, primarily agriculture, under control so that the level of ecological risk in the Dam Lake does not increase. Otherwise, the ecological risk will increase in the dam and sustainable use of the lake will be interrupted. As a result of this study, moderate potential ecological risk was identified in İkizcetepeler Dam Lake based on lithologic properties and anthropogenic activities.

CRediT authorship contribution statement

Şakir Fural: Data curation, Investigation, Methodology, Conceptualization, Resources, Visualization, Writing - original draft. **Serkan Kükrer:** Project administration, Data curation, Investigation, Methodology, Conceptualization, Writing - review & editing. **İsa Cürebal:** Project administration, Funding acquisition, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was carried out with the financial support of Balıkesir University, Scientific Research Projects Unit (BAP). We would like to thank Professor Dr. Ahmet Evren Erginal for supervising the project stage of the study, Furkan Inan for his help in the field work, and Mr. Graham Lee for proof-reading the text.

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